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BOMB DETECTION SYSTEM STUDY

TECHNICAL REPORT

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by

Dr. Andrew Dravnieks

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by A. Dravnieks and H. Weber,

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ABSTRACT

Among the systems that have been proposed for the detection of bombs in air terminals and aircraft, those based on the detection of vapors of explosives have not been sufficiently investigated. The present study was conducted to determine whether suitable vapor-sensing systems are feasible now or in the near future. Common explosives were found to emanate characteristic vapors that could be detected in amounts down to 2×10^{-10} g by using a gas-chromatographic procedure developed for this purpose. A polar stationary phase and an electron-capture detector were employed. The presence of dynamites and other typical explosives in simple geometries could be detected through air analysis in less than 1 min. Most of the common irrelevant contaminants did not interfere with the detection process; a few did to some extent, but routine means which are available can eliminate the interferences. It is concluded that a bomb-sniffer is within the range of foreseeable technology. Development of sampling techniques and escalation of the sensitivity of the analytical subsystem are recommended as the most important future tasks.

2×10^{-10} g

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BOMB DETECTION SYSTEM STUDY

INTRODUCTION

The past and possible future incidents of destruction or damage of aircraft by bombs placed aboard have provided continuous motivation for investigation of means of bomb detection. A survey of effects that accompany the presence of a bomb concealed from sight has been conducted (ref. 1). A device based on the detection of detonator caps tagged with a radioactive source has been built (ref. 2). An analysis of a possible nationwide implementation of bomb detection systems based on detection of tagged caps has been developed (ref. 3), and the possibility of a dynamite bomb explosion without a cap has been experimentally established (ref. 4). Means for preventive explosion of bombs concealed in luggage have also been considered. However, none of the previous work has resulted in a system acceptable for the protection of aircraft against bombing. Hence, the search for detection techniques continues.

Analyzing air for vapors of explosives has been suggested as a means for detection of bombs by chemical methods (ref. 1), but no straightforward chemical detection methods have emerged from past work.

Another suggestion was to use specially trained dogs. Dogs have been trained for other difficult detection tasks such as finding buried explosive mines, weapons, and hidden narcotics. Dogs operate principally on the basis of olfactory sense with possible assistance from other clues.

Because of the element of subjectivity in dealing with animals and the difficulties known to exist in maintaining continuous motivation of dogs to perform the search, this technique was not considered suitable for development for nationwide implementation. However, the principle of detection of bombs by objective olfactory (chemosensing) means would be feasible if instrumental techniques and sensors were available for detection of extremely minute concentrations of characteristic vapors of explosives in air. An objectively operating instrument -- bomb-sniffer -- could then be developed and serve as an artificial dog.

Unfortunately, the sensitivity of a dog's olfactory organs is not yet matched by any instrumental means or sensors when a spectrum of airborne vapors must be read and interpreted. It was felt that if more information about the nature and amounts of the vapors emanated by explosives were obtained, some selective sensing system could be found and adapted to the task of bomb detection. The principal explosives are polynitro compounds and hence strong electron acceptors; it was conjectured that selective sensors could be based on utilization of this or some other molecular characteristic.

The work described in this report was undertaken to answer several questions that arise when considering the feasibility of a bomb detector -- sniffer. What is the nature and amount of vapors emanated by explosives? What is the ability of the existing or nearly existing techniques to detect these vapors in environments less favorable than hermetically closed, uncluttered, containers with impervious walls? What is the ability of these techniques in the presence of other vapors? It was hoped that the answers would enable us to conclude that either the sniffer approach is technologically premature or to recommend course for further research and development.

Accordingly, the Federal Aviation Agency defined the work statement as follows.

A. General Requirements:

"The contractor shall provide all the necessary qualified personnel, supplies, work and equipment to accomplish the following:

1. "Determine whether or not explosives of a character available from the commercial market or manufactured by a simple mechanical or chemical process emanate sufficient amounts of molecules for detection at feasible detection levels.
2. "Explore and report results of the contact potential theory of detecting trace concentrations in atmosphere of varying dimension in the presence of irrelevant trace concentrations.
3. "Upon the conclusion of the foregoing determinations and results and such other additional requirements as may from time to time be authorized or directed by the Contracting Officer under this contract, make recommendations for possible development programs which might be started in the olfactory

field having as a prime objective the discovery of devices to detect explosives before they are introduced into an aircraft.

"Phasing, scheduling and planning of all work shall be subject to such Government control and approval as the Contracting Officer may prescribe."

This report is organized along the lines required in the work statement. Section 1 deals with the answers to item 1 in the work statement. Sections 2-4 discuss various aspects of item 2. Section 5 describes another possible detection technique, based on microwave absorption and investigated when the possibility of this approach occurred during the work. Section 6 presents the discussion of possible implementation of bomb detection systems based on the detection of vapors that emanate from explosives.

1 0 STUDY OF VAPORS EMANATED BY EXPLOSIVES

Detecting explosives by their vapor depends on the concentration of the vapor that is established at the point of air sampling. This concentration depends on thermodynamic and kinetic factors.

The thermodynamic properties of the components of explosives and their mixtures determine the highest vapor concentration that can be reached, for instance, when the explosive is kept for a long time in a container with impervious walls. Chemical species such as nitroglycerin, nitroglycol, etc. possess definite vapor pressures.

Vapor pressure is a function of temperature: this is detailed in Section 1.3.2. When the same chemical species is in a homogenous mixture with other materials or is adsorbed, its vapor pressure is lower. Thus, the vapor pressure of nitroglycerin in gel with nitrocellulose, or of dinitrotoluene in solid solution with trinitrotoluene, is lower than that of the pure compounds. Dilution and intermolecular interaction cause the reduction in vapor pressure. To determine whether an explosive can be detected through its vapor, it is necessary to know the vapor pressures that correspond to various temperatures. The vapor pressures in mixtures rarely follow the laws of ideal mixtures in which pressure is proportional to concentration because molecular interactions exist between the components of the mixture. Polynitro compounds are strong electron donors, and the nitro groups have high dipole moments. Therefore polynitro molecules

can be expected to interact strongly with many other substances, and deviations from the laws of ideal mixtures should be a common occurrence. Under these conditions, only direct experimental measurements on explosives can supply reliable vapor pressure data.

When an explosive is brought into an environment that is initially free of the explosive's vapor, the explosive continues to evaporate, and the concentration of the vapor in the environment gradually increases. Here, kinetic factors co-determine the vapor concentration. The rate of emission depends on the vapor pressure of the explosive and the aerodynamic conditions in the vicinity of the explosive's surface. Thus, if the vapor pressure is low, the rate of its accumulation in the environment is also low. If another process is simultaneously operative by which the vapor can disappear from the environment, the saturation concentration will never be attained. Instead, a steady-state concentration is established when the rate of disappearance equals the rate of emission. The disappearance process can consist of leakage to some other environment or sorption on surfaces of solids and solution in organic materials.

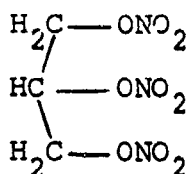
Thus, in a generalized environment the concentration of the explosive's vapor can be lower than explosive's equilibrium vapor pressure. The rate of concentration buildup depends on the vapor pressure which is a characteristic of the explosive and on the environment which determines the temperature and the dissipation rate. This section presents the data and experimental results on the types of vapors emitted by pertinent explosives and on the vapor pressures of the components of the explosives separately and in several compound explosives. The influence of the environment is discussed in more detail in Section 2.

1.1 Types of Explosives

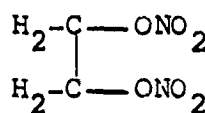
Whoever intends to place a bomb on aircraft can obtain explosives from several sources. Simple inexpensive explosives are distributed commercially and can be purchased or stolen. More specialized military explosives can be bought as surplus materials or stolen. Both can be supplied from abroad. Finally, some explosives can be prepared from readily commercially accessible materials.

A survey of the literature (ref. 5), previous reports prepared by prior research contractors for the Federal Aviation Agency and Air Transport Association, and discussions with Dr. R. W. Lawrence, Hercules Powder Company, Wilmington, Delaware, helped list the principal classes of explosives for this study.

Dynamites have been used in all past bombings. Although some military dynamites can be based on trinitrotoluene (TNT) and contain no nitroglycerin, nitroglycerin is one of the principal components in most dynamites, especially in general commerce. The nitroglycerin in these actually is usually a mixture of the nitroglycerin proper (I) and nitroglycol (II) (ethyleneglycol dinitrate, EGDN)



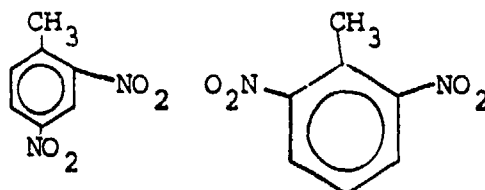
I



II

The content of nitroglycol in this type of nitroglycerin may be up to 80%. Nitroglycol serves as a functional component; however, every technical nitroglycerin, unless specially purified, contains nitroglycol. Other components of dynamites are ammonium or sodium nitrates and carbonaceous ingredients -- wood flour, ground nutshells, starch, cornflour, bagasse, etc. Sometimes, minor amounts of nitrocellulose or dinitrotoluene can also be present.

Dinitrotoluenes:

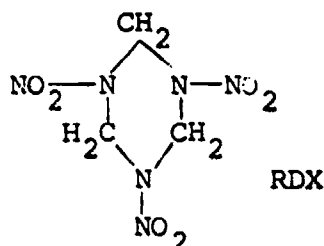
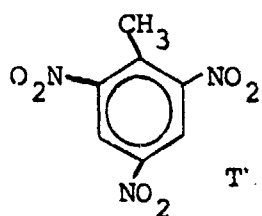


Dynamites are usually detonated by a blasting cap. However, alternative methods of detonation, e.g., through the use of a PETN primer cord (pentaerythritol tetranitrate, ref. 4), have been demonstrated, indicating that tagging of the caps with a radioactive or other tracer would not be a sure way for the detection of bombs based on dynamite. The dynamite sticks are manufactured with a wax paper or polyethylene film wrapping.

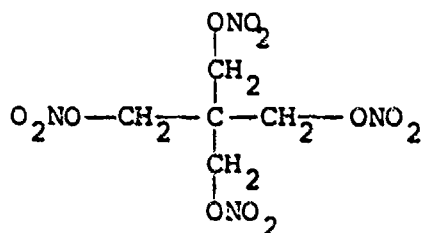
Carbonitrates are commonly used in the blasting industry. Commercially distributed varieties typically contain 90% or more ammonium nitrate and several percent of organic components such as coal powder and paraffin. As a functional additive, dinitrotoluene may be present at the 5% level. It is becoming common that blasting contractors prepare their own explosive by mixing, e.g., 94% of ammonium nitrate with 6% fuel oil. Approximately one-half of the explosives used in the blasting industry is made in this way. Explosives of this type cannot be exploded without the use of a booster, which typically is dynamite or a composition based on TNT.

Smokeless powders are explosives normally used in shotgun powders and can vary widely in composition. Nitrocellulose is the major component. Dinitrotoluene (DNT) is introduced into the grain coating to control the rate of burning, except for large-grain types. Nitroglycerin (nitroglycerin + nitroglycol) can be present in double-base powders, and nitroguanidine is further added in triple-base powders. Other components are added: diamyl, butyl or ethyl phthalates as plastisizers, and diphenylamine, 2-nitrodiphenylamine, or diethylphenylurea as stabilizers.

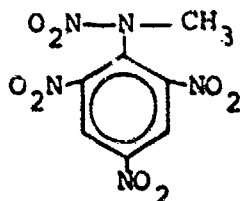
Military explosives vary much more in formulation. Trinitrotoluene (TNT) and N,N,N-Trinitromelamine (RDX)



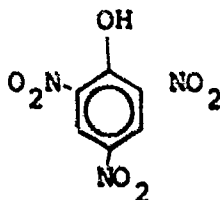
are the most common components. Other components may be pentaerythritol tetranitrate (PETN)



tetryl



and in minor amounts, picric acid



or ammonium picrate.

Dynamite, smokeless powder, and the other compositions mentioned above are also widely used in military applications.

Slurry powders contain water, in addition to TNT or smokeless powder, and ammonium and sodium nitrates.

Black powder is a low-power explosive and typically contains 74% potassium nitrate, 16% charcoal, and 10% sulfur.

Boosters are used to initiate the less sensitive explosives that cannot be initiated directly with a cap. Boosters can be a stick ($\frac{1}{2}$ lb) of dynamite, or a charge of Composition B consisting of TNT and PDX, or a similar TNT-containing explosive. From 1 oz to 1 lb of a booster may be needed depending on the explosive to be initiated.

Detonating fuses or primer cords usually are based primarily on PETN.

Homemade explosives can be of several types. It is unlikely that nitroglycerin, TNT, or another primary explosive will be synthesized by a saboteur; these processes require considerable know-how and chemical equipment, and even a person sufficiently skilled in this field will not be inclined to undertake the risky process except under very unusual circumstances.

Black powder is an obvious choice and has been so in nuisance bombings of places of business. Its components are easily available and the explosion is easily initiated. However, previous studies have shown that amounts smaller than 15 to 20 lb are not likely to destroy a jetliner, and in most locations in passenger jetliners where large charges could be placed clandestinely, more than 30 to 40 lb would be needed.

Ammonium nitrate-based explosives can be even more easily prepared, e.g., from fuel oil and the fertilizer-grade ammonium nitrate. These explosives are sufficiently strong but must be initiated with the assistance of a dynamite- or TNT-containing booster. Hence, detection of homemade ammonium nitrate type of bomb should be possible through detection of a booster.

Nitrostarch, instead of nitroglycerin, is used by the Trojan Powder Company.

1.2 Selection of Samples

The review in the previous section indicated that, although many formulations exist, a system that could detect a few selected chemical species would be able to protect against almost any conceivable high-destructivity bomb. The principal selected species are nitroglycol, nitroglycerin, TNT, and DNT.

Dr. R. W. Lawrence, Hercules Powder Company, assisted in selecting typical explosives for use in the detection study. These explosives were:

- (1) Gelamite I (represents dynamite) -- contains 20% nitroglycerin (including nitroglycol), 65% ammonium nitrate, 7% sodium nitrate, and 8% carbonaceous materials. Form: sticks, 8 in. long, 1 $\frac{1}{4}$ -in. diameter, in a wax paper wrapper.
- (2) Vibronite B (represents commercial ammonium nitrate based explosive) -- contains 91% ammonium nitrate coated with 0.5% zinc stearate or rosinate, 5% DNT, and 4% ground coal.
- (3) Composition B (used in boosters, typical of military explosives) -- contains RDX + TNT.
- (4) 40-mm Powder (represents smokeless powders) -- contains DNT in coating and nitroglycerin, including nitroglycol.
- (5) Homemade Explosive -- prepared at IITRI by mixing ammonium nitrate with No. 6 fuel oil.

Other explosives used in this study were:

- (6) Gelobel C (dynamite) -- contains 15 to 20% nitroglycerin (consisting of 60 to 80% nitroglycol and 40 to 20% nitroglycerin), 65% ammonium nitrate, 10% sodium chloride, and carbonaceous material.
- (7) Monobel SA (dynamite) -- contains 9% nitroglycerin (composed as in Gelobel C above), 75% ammonium nitrate, 8 to 9% sodium chloride; the rest is carbonaceous material.

In addition, the following chemicals and preparations were used in the study:

- (8) Trinitrotoluene, Eastman-Kodak, indicator-grade.
- (9) 2,4-Dinitrotoluene, Eastman-Kodak, white-label grade.
- (10) Nitroglycerin, prepared in IITRI laboratories by Mr. T. Erikson.

- (11) Medicinal nitroglycerin tablets, known to consist principally of starch with chemically pure nitroglycerin.
- (12) Solution of 1% nitroglycol in acetone.
- (13) Solution of 1% nitroglycerin, without nitroglycol, in acetone.

The two last samples were prepared for IITRI by the Hercules Powder Company. The assistance of Dr. Lawrence in arranging for these samples as well as in supplying the explosives 1 through 7 is gratefully acknowledged.

1.3 Available Data on Vapor Pressures

A survey of various sources was conducted to collect existing information on the vapor pressures of explosives; additional data were derived through thermodynamic relations.

1.3.1 Existing Data

A survey of the literature and inquiries with the Hercules Powder Company and Picatinny Arsenal established that no data exist on the vapor pressure of the separate components of explosives when they are co-present in complex explosives. Some data were available for the nominally pure components, but of unknown purity. Figure 1 compiles the known values of the vapor pressures in a plot of $\log p$ versus reciprocal temperature; interpolations and extrapolations are possible in this plot because of classical thermodynamic relations. No data for dinitrotoluene were found. Further data for TNT can be predicted from the thermodynamic relations (Section 1.3.2).

1.3.2 Extrapolation of TNT Vapor Pressure Data

The only vapor pressure data on TNT available are those above its melting point. It is well known that the rate of change of the vapor pressure with the temperature of the solids is always greater than that of the corresponding liquids. Hence the data for liquid TNT cannot be directly extrapolated to room temperature.

A good approximation to the vapor pressure behavior of TNT in the solid range can be obtained from two thermodynamics relationships. The Clausius-Clayperon equation gives the logarithm of vapor pressure as a function of the heat of vaporization:

$$\log_{10} P_1 = - \frac{\Delta H_v}{2.303 R T} + C \quad (1.3.2-1)$$

where

$\log_{10} P_1$ is the decimal base logarithm of the vapor pressure of the liquid

ΔH_v is the heat of vaporization of the liquid, cal/mole

R is the universal gas constant, 1.987 cal/mole $^{\circ}K$

T is the absolute temperature, $^{\circ}K$

C is a numerical constant dependent on the units chosen for P_1 .

The second equation relates the heat of sublimation of the solid to the heat of vaporization of the liquid.

$$\Delta H_s = \Delta H_v + \Delta H_f \quad (1.3.2.-2)$$

where

ΔH_s is the heat of sublimation of the solid, cal/mole

ΔH_f is the heat of fusion of the solid, cal/mole.

This equation is strictly true only at the melting point of the substance. However, the change in ΔH_s is small as the temperature is lowered.

To estimate the vapor pressure of solid TNT, the heat of sublimation is used in the Clausius-Clayperon equation instead of the heat of vaporization. Hence,

$$\log_{10} P_s = - \frac{\Delta H_s}{2.303 R T} + C \quad (1.3.2.-3)$$

where P_s is the vapor pressure of solid TNT, and the other terms are as defined previously. ΔH_v is estimated from the known liquid vapor pressure data, and ΔH_f is known from calorimetric measurements (ref. 5, p. 267); added together, (Equation 1.3.2.-2) they give ΔH_s . It was in this way that the lower branch (labelled 6A) of the TNT curve shown in Figure 1 was obtained.

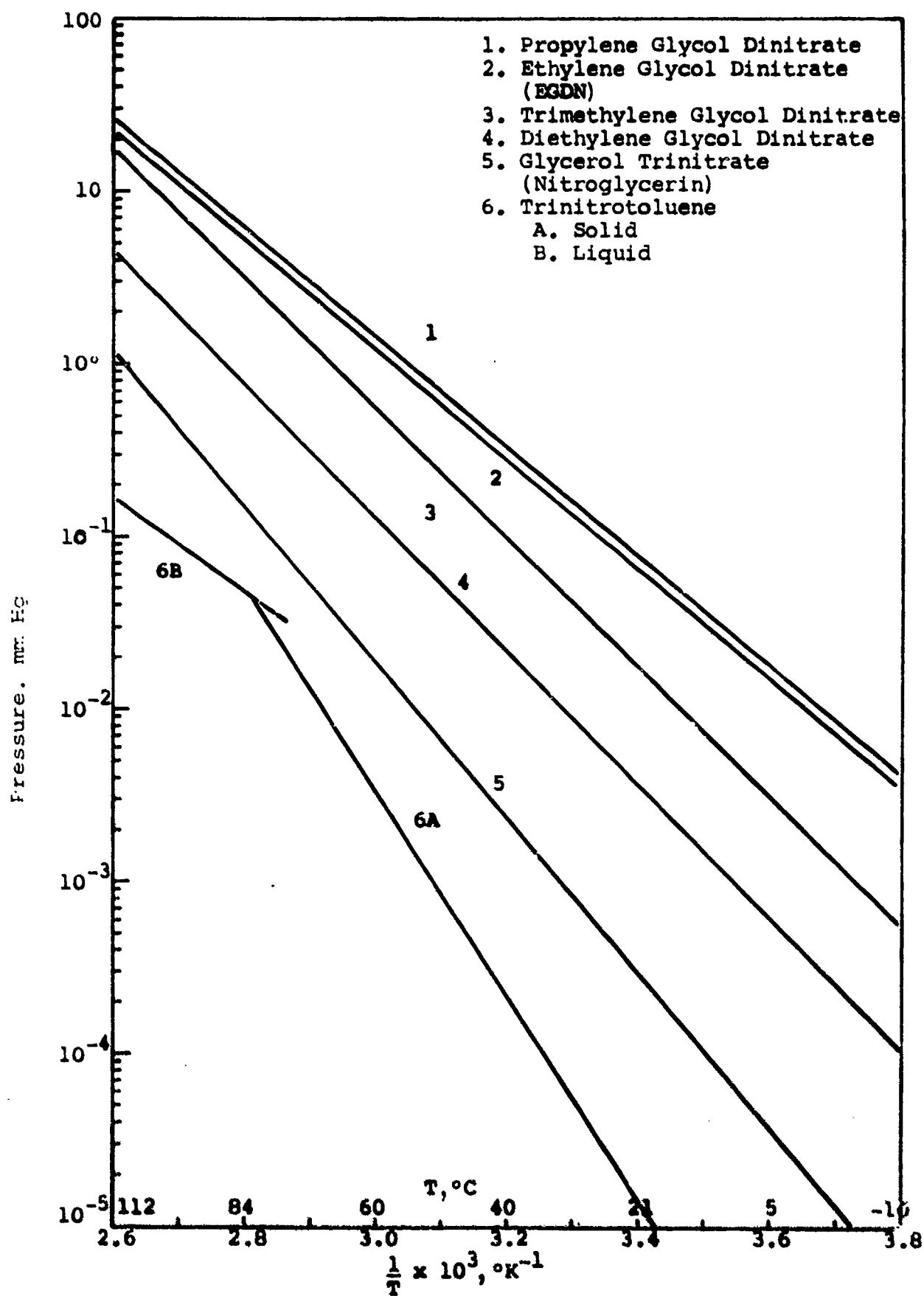


Figure 1. KNOWN VAPOR PRESSURE DATA FOR EXPLOSIVES

1.4 Choice of Experimental Methods

Since no data were available in the present art on the vapor pressures of DNT and of the components of complex explosives in mixtures with others, and since the necessary data could not be theoretically derived, experimental techniques had to be selected for obtaining the vapor pressures empirically.

A dozen or more experimental techniques can be used to measure vapor pressure, and each is suited to the chemical nature of the materials and the pressure range to be studied. Two general techniques especially useful for low-vapor-pressure compounds, such as those that occur in explosives, are the effusion methods and the flow methods.

In effusion methods the substance is placed in a glass bulb with a small (0.5 mm) hole but otherwise continuous. The bulb is then mounted in a vacuum chamber that can be held at any desired temperature. Molecules escaping through the small hole condense on a nearby coldplate and are completely trapped there. A number of methods can be used to measure the amount collected, including direct weighing. Although it is possible to attain great accuracy with these methods, it is evident that a rather elaborate apparatus is required for success, and work with complex mixtures is not possible since several components can escape simultaneously.

For our work a simpler, but less accurate, transport method was chosen. The method can be readily described by referring to Figure 2. The substance, S, to be studied is placed in a U-shaped tube in a thermostat, T. The tube has a capillary constriction at C to reduce the counterdiffusion of vapor molecules back to S.

Very pure helium gas from the tank, G, is fed through a liquid nitrogen-cooled trap to remove residual contaminants and through the U-tube where it picks up the vapors from S. It then passes through the heated tube, H, to the cold trap in the Dewar, D. Here, all the vapor molecules are frozen out, while the gas passes on through the flowmeter, F.

The amount of vapor collected is then measured as follows. The U-tube is removed from the gas train and rinsed with 1-ml aliquots of pure acetone 3 times. These are poured into a 10-ml volumetric flask, which is then filled to its calibration mark. A 1 to 10 μ liter* sample of this solution is injected into a gas chromatograph for identification and analysis. The chromatograph (described in Section 1.5) is calibrated by making up known solutions of the substance being studied and running them through under the same conditions as the unknown samples.

* $1 \mu\text{liter} = 10^{-6}$ liter

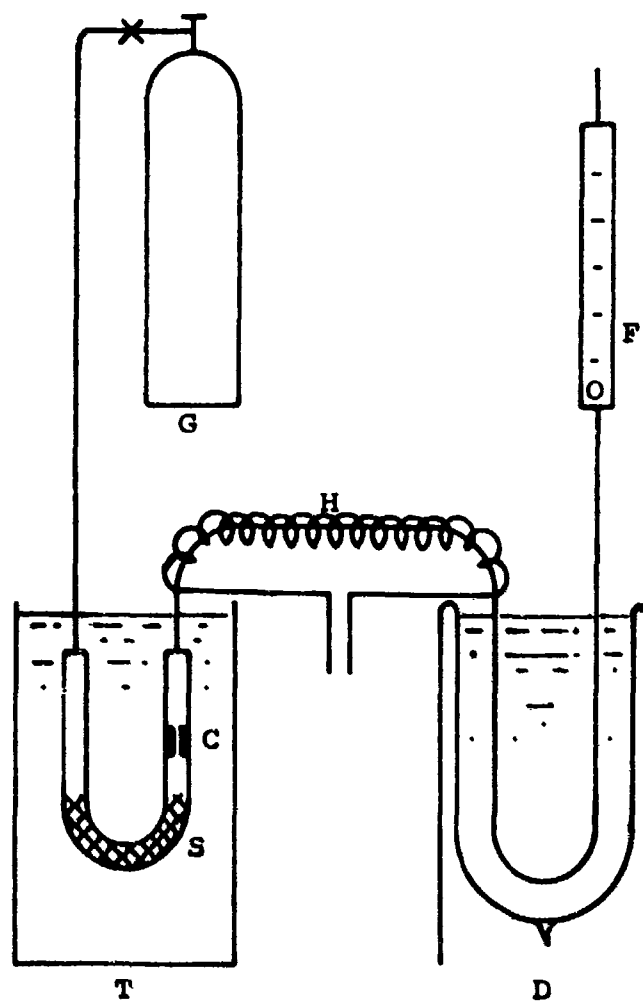


Figure 2

SCHEMATIC DIAGRAM
OF
TRANSPORT VAPOR PRESSURE APPARATUS

From the flow rate and time of flow the volume, V, of gas that passed over the sample is known. The chromatograph yields the amount of vapor, m, in that volume. The vapor pressure is calculated from the perfect gas law:

$$P = \frac{m R T}{M V}$$

where P is the vapor pressure, M is the molecular weight of the vapor molecules, R is the universal gas constant, and T is the absolute temperature of the exit gas (usually 298°K).

1.5 Development of the Gas Chromatographic Technique for Explosive Vapor Analysis

In this section the principles and processes involved in gas chromatography (GC) will be briefly described. Also, the development of an effective analytical technique for explosive vapor analysis will be indicated.

1.5.1 Principles of Gas Chromatography

Gas chromatography is an important tool in chemical analysis; it is closely related to fractional distillation. In it a dilute solution of the sample to be analyzed is injected into a heated metal block (FV in Figure 3)*and instantaneously volatilized. A pure carrier gas from the tank, T, then sweeps the vaporized sample into a long column, C, coated inside with a thin film of nonvolatile liquid, called a stationary phase.

In the column the chemical components of the sample are separated into bands. Each band moves at a different rate through the column, thus effectively separating the different types of molecules in the sample. The total time required by the band to pass through the column is called the retention time of that band. The retention time of a given molecular species is characteristic of and different from that of almost all other species. Thus, interferences and misinterpretations are low in this technique. The basic factor that determines the retention time is the partition coefficient. It expresses mathematically the distribution of the analyzed substance between vapor phase and the stationary liquid phase. The partition coefficient is a characteristic number for the combination of the given chemical species and stationary phase.

As the molecules emerge from the column, a detector, D, at the exit measures their concentration in the carrier gas. The detector gives an electrical signal that is amplified and recorded.

*See Appendix for a photograph of the laboratory equipment.

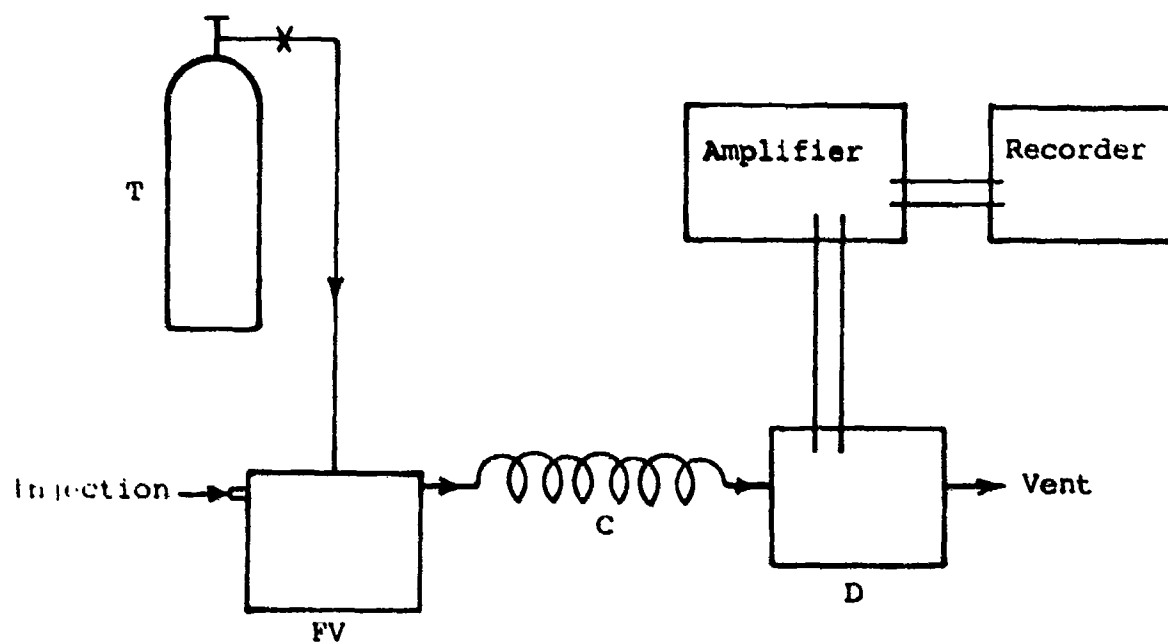


Figure 3
SCHEMATIC DIAGRAM OF ESSENTIAL PARTS
OF
A GAS CHROMATOGRAPH

In this way samples of widely varying character can be analyzed and identified. A complete discussion of this subject can be found in Chapter 1 of reference 20.

1.5.2 Development of Gas Chromatographic Technique for Explosive Vapors

Examination of standard references and discussion with several explosive manufacturers revealed little information on the GC analysis of the expected explosive vapors. Initial attempts to detect TNT on a standard column used for similar compounds failed. Such columns are usually about 10 ft long and tightly packed with coated particles to give excellent but lengthy separations. The low-vapor-pressure TNT molecules would not emerge in the 30 to 45 minutes usually required to get a good chromatogram. Raising the temperature of the column to speed up the process failed because the TNT decomposed on the column.

Therefore, it was decided to work with a short (15 in.) column with an inside diameter of 3 mm and no packing. The column was coated with a thin layer of Carbowax 20M, a polyglycol wax which is effective in separating polar compounds such as alcohols, ether, and ketones.

Another important factor in obtaining good chromatograms is the detector used. The three most sensitive detectors in use today are flame ionization, argon ionization, and electron capture; the electron-capture detector was chosen because it is particularly sensitive to those compounds which readily form negative ions by capturing free electrons, such as the nitro and nitrate compounds in dynamites. The flame-ionization detector is not as sensitive, and the argon-ionization detector is not as specific as the electron-capture device.

Other factors affecting the analysis, such as carrier gas flow rate, column temperature, solvent, and sample volume, were worked out in a series of preliminary experiments. First, water was tried as a solvent for TNT. This led to rapid deterioration of the column, probably due to formation of nitric acid upon partial decomposition of the TNT. Methyl alcohol and acetone proved to be the best solvents. Since they are very volatile, they pass rapidly through the column. Benzene was also useful in certain experiments.

1.5.3 Final Tentative Procedure

The conditions used to analyze various explosive vapor components are given in Table I. In general, it was found that ethylene glycol dinitrate was readily detected, as was

TABLE I
DATA FOR ANALYSIS OF EXPLOSIVE COMPONENT VAPORS

Compound	Column Temperature, °C	Retention Time, min	Mass Required to Give Signal-to- Noise Ratio of 1:1, nanograms
Ethylene glycol di- nitrate (EGDN)	72.5	0.25	0.28
Glycerol trinitrate (nitroglycerin)	62	1.55	0.15
2,4-dinitro- toluene (DNT)	93	1.0	0.5
2,4,6-trinitro- toluene (TNT)	105	2.4	0.5

CONDITIONS: COLUMN -- 15 in. long x 3-mm OD, Pyrex, coated
with Carbowax 20M from 10% trichloro-
ethylene solution

CARRIER GAS -- 30 cc/min, ultrapure helium

DETECTOR -- Electron-capture

CHROMATOGRAPH -- Burrell Corporation, Model K.

2,4-dinitrotoluene. Nitroglycerin and 2,4,6-trinitrotoluene were much more difficult to collect. This effect is discussed in Section 1.6.2.

In summary, the chromatograph was set up according to Table I, depending on what compound was to be studied. Whenever possible, known standard solutions were run before unknowns to calibrate the detector. Samples collected by the flow method or by various other ways were diluted to 10 ml with acetone or benzene and analyzed. In some experiments, however, it was possible to obtain small air samples (about 3.0 cc) and to inject them directly into the chromatograph with suitable results.

1.6 Vapor Pressure Measurements on Explosives

1.6.1 Measurements on Pure Materials

Since trinitrotoluene is one of the simplest, best-known and most important constituents of many explosives, it was the first one chosen for study. Vapor-pressure data measured on a sample of Eastman Kodak Company indicator-grade 2,4,6-trinitrotoluene are presented in Figure 4. This highly purified material still contained enough 2,4-dinitrotoluene (DNT) as an impurity, which could be more easily detected than the TNT. Therefore, the DNT was analyzed as an impurity in the TNT vapor and graphed with the TNT in Figure 4. The measurements on pure DNT are also presented. The reduction of DNT vapor pressure by a factor of 50 at 39°C indicates a concentration of about 2% or less in the pure TNT. Since TNT is made by the direct nitration of toluene, which passes through the mono and dinitro stages, such an impurity level is expected.

As seen from Equations 1.3.2-1 and 1.3.2-3, the vapor pressure-temperature measurements on a pure substance, liquid or solid, generally result in straight-line plots when $\log P$ is plotted vs. $1/T$. However, with mixtures of materials, this simple relation no longer holds due to specific molecular interactions, changing composition, and heat of solution effects. Hence, the pronounced curvature of the DNT impurity curve (A symbol in Figure 4) is not unexpected. Depletion of DNT in the surface of TNT sample at higher temperature also can cause similar deviation.

Figure 5 indicates the effect of flow rate on the measured vapor pressure of TNT at 70°C. As the flow rate increased, some of the carrier gas passed over the solid without establishing full equilibrium, thus resulting in a vapor-pressure measurement that was lower than expected. This is

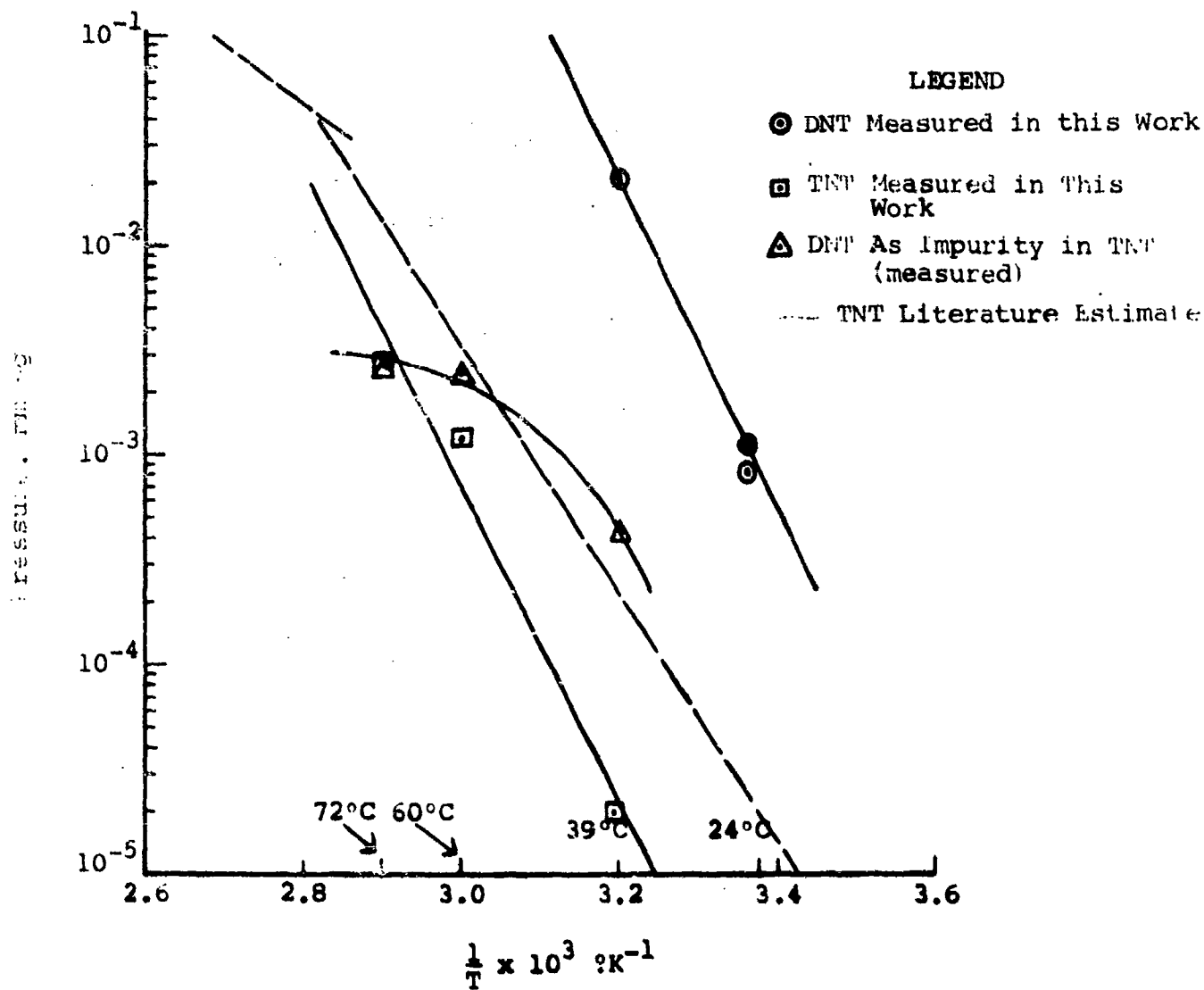


Figure 4

VAPOR PRESSURE VS. RECIPROCAL ABSOLUTE TEMPERATURE
FOR TNT, DNT, AND DNT AS AN IMPURITY IN TNT

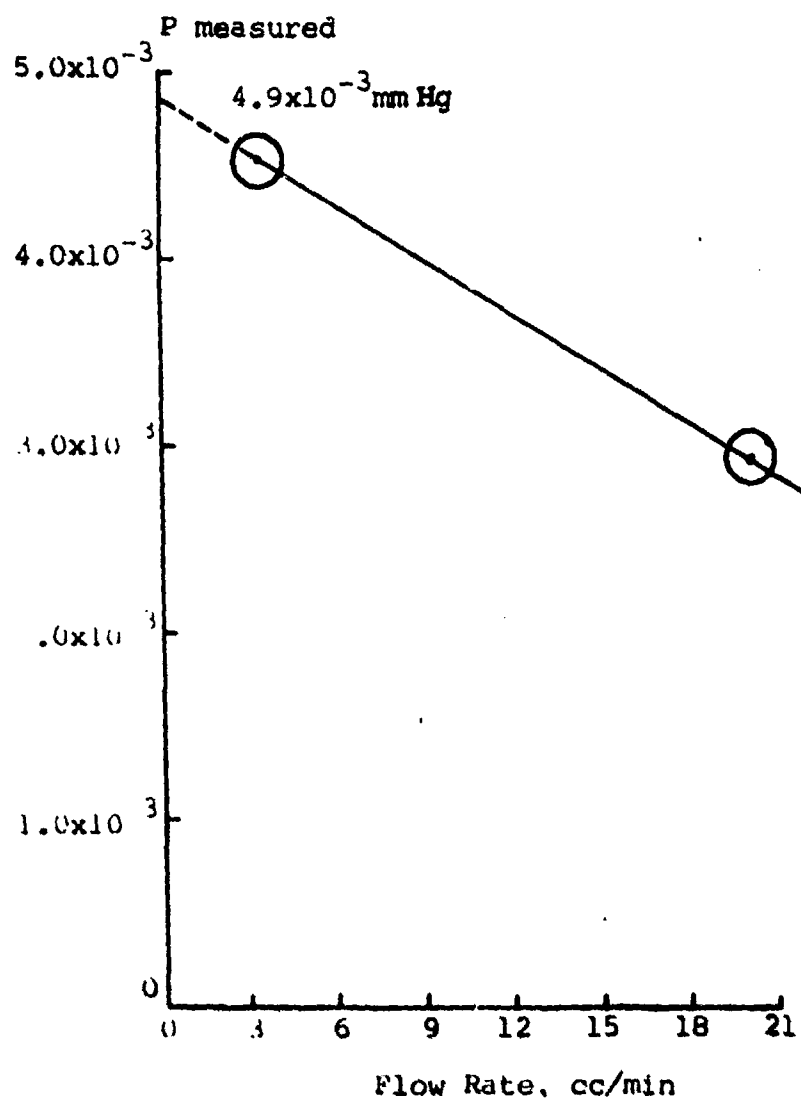


Figure 5

MEASURED PRESSURE VS. FLOW RATE
FOR TNT AT 70°C

the main reason the flow method is considered less accurate than the effusion or static methods of vapor pressure measurement. However, the error caused by unsaturation is not sufficient to influence the soundness of further considerations on bomb detection.

As shown in Figure 4, TNT has a very low vapor pressure, about 10^{-5} mm Hg at room temperature. This means that 10 to 20 hr of flow is required to collect enough material for an accurate measurement of its vapor pressure over any mixture. Since DNT always occurs as an impurity in TNT or is added to explosive mixtures to modify their explosive properties, experiments on an actual explosive powder were performed with analysis of the condensate for DNT as discussed below.

1.6.2 Vapor Pressure of DNT over Composition B Explosive

Composition B is a dynamite formula typical of military explosives consisting of 40% TNT and 60% Cyclonite (RDX) with DNT as an impurity. Samples were obtained in block form and in a fine-powder mixture. The physical form of the explosive is very important in determining the rate at which the equilibrium vapor pressure of each of the components is established in any particular geometry.

In Figure 6 the measured vapor pressure of pure DNT is compared with DNT in fine-powder Composition B, DNT in block-form Composition B, DNT in purified TNT, and pure TNT, all at 39°C. The DNT vapor pressure in fine-powder Composition B is reduced by a factor of about 10 by dilution in the TNT and Cyclonite. The block form does not establish equilibrium rapidly enough for the same flow conditions, and the DNT vapor pressure appears to be about 60 times less than that of the pure material. This happens to be about that observed in purified TNT. For comparison, the observed vapor pressure of TNT at 39°C is included. It is about 1000 times less than that of pure DNT, which is a good indication of why it is much easier to observe DNT vapors even when they appear only as impurities.

1.6.3 Experiments on Nitroglycol-Containing Explosives

Another common explosive constituent is ethylene glycol dinitrate (EGDN), called nitroglycol in the trade. Technical nitroglycerin contains this material in proportions varying from 20 to 80%. Because of its relatively high vapor pressure, it is easy to collect and measure. Measurements on Du Pont Gelobel-C, which contains 14% EGDN, showed a vapor pressure of 1.8×10^{-2} mm Hg compared to 8.0×10^{-2} mm Hg for the pure compound at 24°C (room temperature). This reduction by about 80% in vapor pressure is expected from the dilution and interaction with the other components, as with DNT in Composition B.

Also, because of the high vapor pressure of EGDN, it is easy to detect this vapor directly in air (Section 3.0).

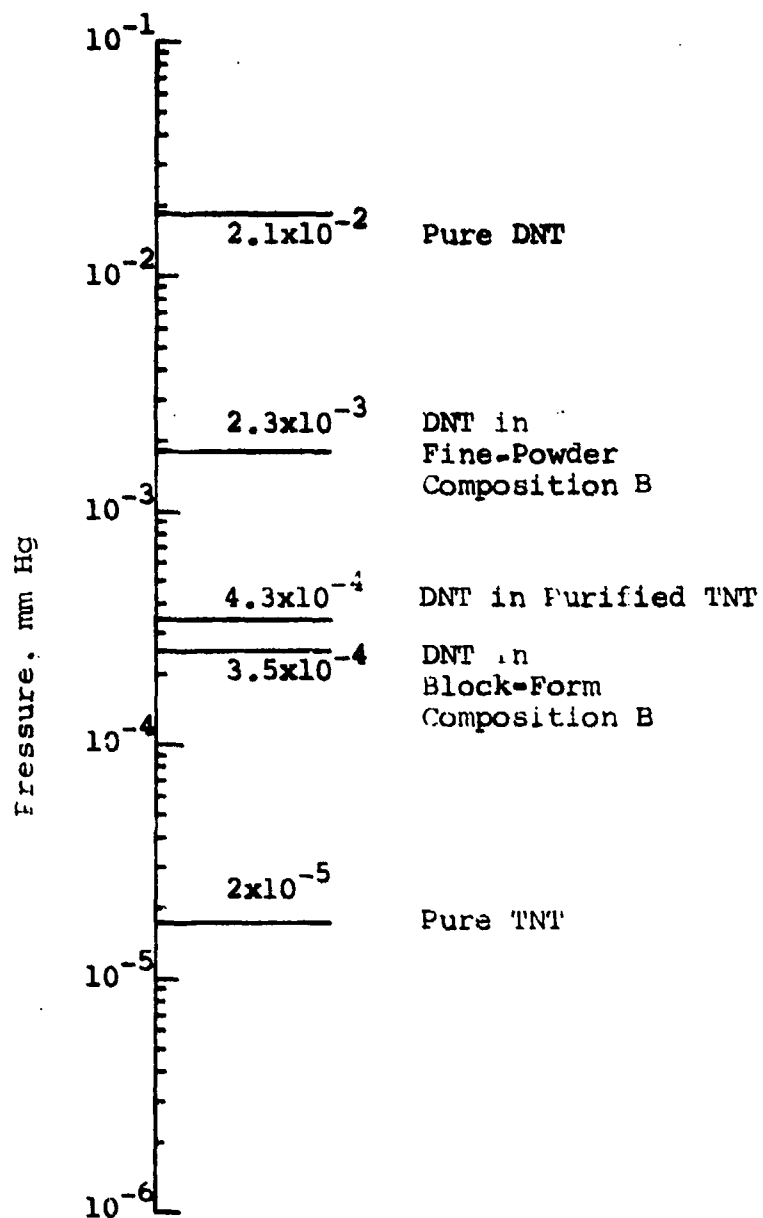


Figure 6

DNT VAPOR PRESSURES COMPARED

2.0 CONTACT-POTENTIAL DETECTOR STUDY

For selective high-sensitivity detection of the vapors of the explosives the detector must utilize some characteristic molecular property of the explosive. As shown in Section 1, explosives emanate vapors of polynitro and organic nitrate compounds. Among these, nitroglycol and dinitrotoluene are the most promising components for use in detection since their volatility is higher than that of other components of the explosives.

Both substances are polar.* Also, the presence of nitro groups and, in the case of DNT, the combination of the nitro groups and the electronic structure of the benzene ring of the molecule make both substances good electron acceptors. Since the majority of volatile substances are polar, the polarity of the nitroglycol and DNT represents a relatively common characteristic. The property of being an electron acceptor is, however, much less common. This property was utilized in the electron-capture detector described in connection with the gas-chromatographic detection.

Another possibility of characteristic detection of electron acceptors exists in their ability to form charge-transfer complexes with good electron donors.

2.1 Charge-Transfer Complexes -- Literature

Electron donors can be found among molecules such as polynuclear aromatics; complexes of TNT with naphthalene (ref. 6,7), picryl chloride (ref. 6), and carbazole (ref. 8,9) have been found. Donor stilbene has been reported to combine with the acceptor *s*-trinitrobenzene (ref. 10). Other electron donors not yet investigated in relation to the polynitro compounds are disulfides (ref. 11,12), amides (ref. 12,13), sulfur, and selenium analogs of dioxane (ref. 14). Biologically active or relevant substances that are strong electron donors include, e.g., chlorpromazine (Thorazine) and carotenes. Tabulations of the electron-donating characteristics of many compounds are available (ref. 15,17)..

The choice of means for detecting the charge-transfer complex formation was considered. The calculations used by the authors of this report have been made in conjunction with a paper prepared early in 1964 (ref. 18). The detector must be able to indicate the presence of small amounts of the complex formed. The amount of the complex in a small volume of a condensed phase forms as follows:

* See Section 5.0 for a discussion of polar molecules.



and at equilibrium

$$C_{AD} = C_A C_D K$$

$$\Delta G = -R T \ln K = -1.4 \log_{10} K$$

Here C is the corresponding concentration, K is the equilibrium constant, and ΔG is the free energy of formation of the complex shown for the case of 27°C (300°K) temperature by the last term. The values of K for the common values of ΔG are in the range of 10 to 1000. A good excess of the donor can be provided, since this is the sensor. However, C_A , the concentration of the acceptor (e.g., nitroglycol), will be low if sensitive detection is desired. Hence, only a fraction of the donor molecules will usually enter the complex. Detection by color changes, in spite of the usually intensive coloring and high extinction coefficient of the complexes, was shown to be rather insensitive; a package of 1×10^{11} molecules is approximately the smallest amount that would be detected even in a favorable case.

Another technique of detection can be based on the frequently high dipole moment of the complex. This technique and some results obtained with it are described in the following section.

2.2 Contact Potentials and Their Measurement

The term contact potential describes the potential that has to be applied between two conducting plates to compensate the electric field that exists in the gap between the plates (ref.19). One plate is usually chosen so that its contribution to the contact potential is relatively constant and independent of air contaminants. The other plate, the sensor, is chosen so that its surface potential -- a component that forms a part of the contact potential -- responds selectively to presence of a vapor.

The principal surface potential change at ambient temperatures occurs when polar molecules adsorb at the sensor surface with a certain degree of orientation. The magnitude of the surface potential and consequently of the contact potential change is then:

$$\Delta E = 3.77 \times 10^{-15} n \cdot \mu \quad 2.2-1$$

Here n is the number of polar molecules per cm^2 of the sensor's projected surface and μ is the average dipole moment, in Debye units, of adsorbed molecules in direction normal to the sensor surface.

The polynitro compounds are polar and produce contact-potential changes on adsorbing and orienting sensors. However, the ability of

the polynitro compounds to form high-dipole moment charge-transfer complexes was considered as a possible basis for more specific sensors. The principle of the hypothetical sensor is shown in Figure 7. The sensor consists of a metal surface coated with an electron donor. The molecules of TNT adsorb on the donor layer and there produce a charge-transfer complex oriented with the dipole normal to the surface. This should change the surface potential and the contact potential of the sensor with respect to the reference plate (not shown).

Experiments on the possibility of detecting vapors of explosives in such a fashion were conducted in the contact-potential measuring apparatus shown in Figures 8 and 9. The reference plate or electrode is a gold-coated prealuminized Mylar* diaphragm vibrated pneumatically by air pulses at 120 cps from a membrane-type aquarium air pump. The gold-disc electrode receives the coating of the sensor substance. Vibration of the reference electrode generates an AC signal in the circuit connecting the electrodes. This signal is detected by an oscilloscope. The contact potential is measured by adjusting the ground-to-sensor potential until the signal on the oscilloscope disappears. Changes in the signal can be recorded as changes in the value of the rectified signal taken from the oscilloscope. The contact potentials could be measured within ± 2 mv. See the Appendix for a photograph of the laboratory equipment.

2.3 Exploration of Contact-Potential Sensors

The exploration of sensors based on the formation of adsorbed charge-transfer complexes was conducted concurrently with the early stage of the vapor emanation study. It was soon found that the electron-capture detector, also based on the electron affinity of polynitro compounds, is a very sensitive tool for detection of small amounts of such compounds. Thus the exploration of the contact-potential sensors consisted of two phases: experimental exploration and theoretical comparison with the present capabilities of the electron-capture detector.

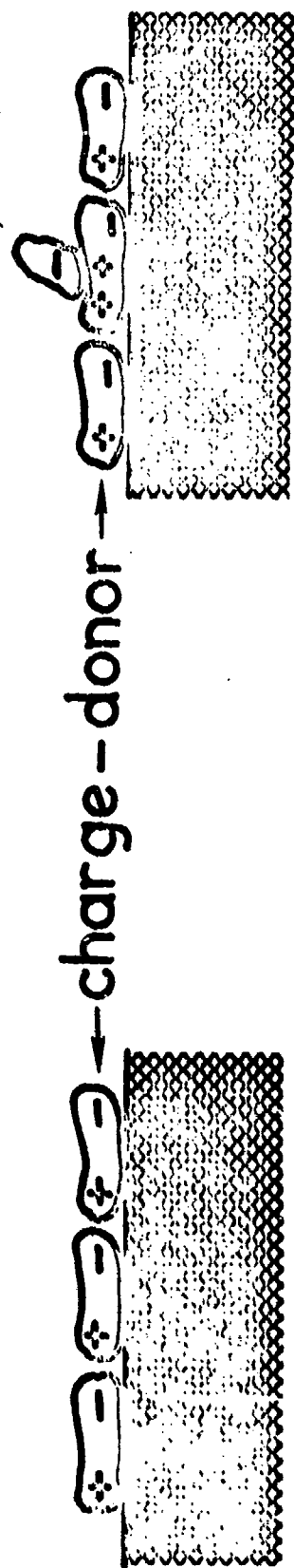
2.3.1 Experiments

Some experiments were conducted with 2,4-dinitrotoluene (DNT) vapor on a sensor substrate that from past work was known to have high adsorptivity for polar and hydrogen-binding molecules. This substrate is a thin coat of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, deposited by fast evaporation of a drop of saturated aqueous solution of calcium sulfate on a gold support (cleaned by brushing with a hydrogen flame just before coating). The nitrogen stream was delivered

* Du Pont Company polyester film.

AIR

AIR + CONTAMINANT



CHARGE-DONOR SENSOR

Figure 7

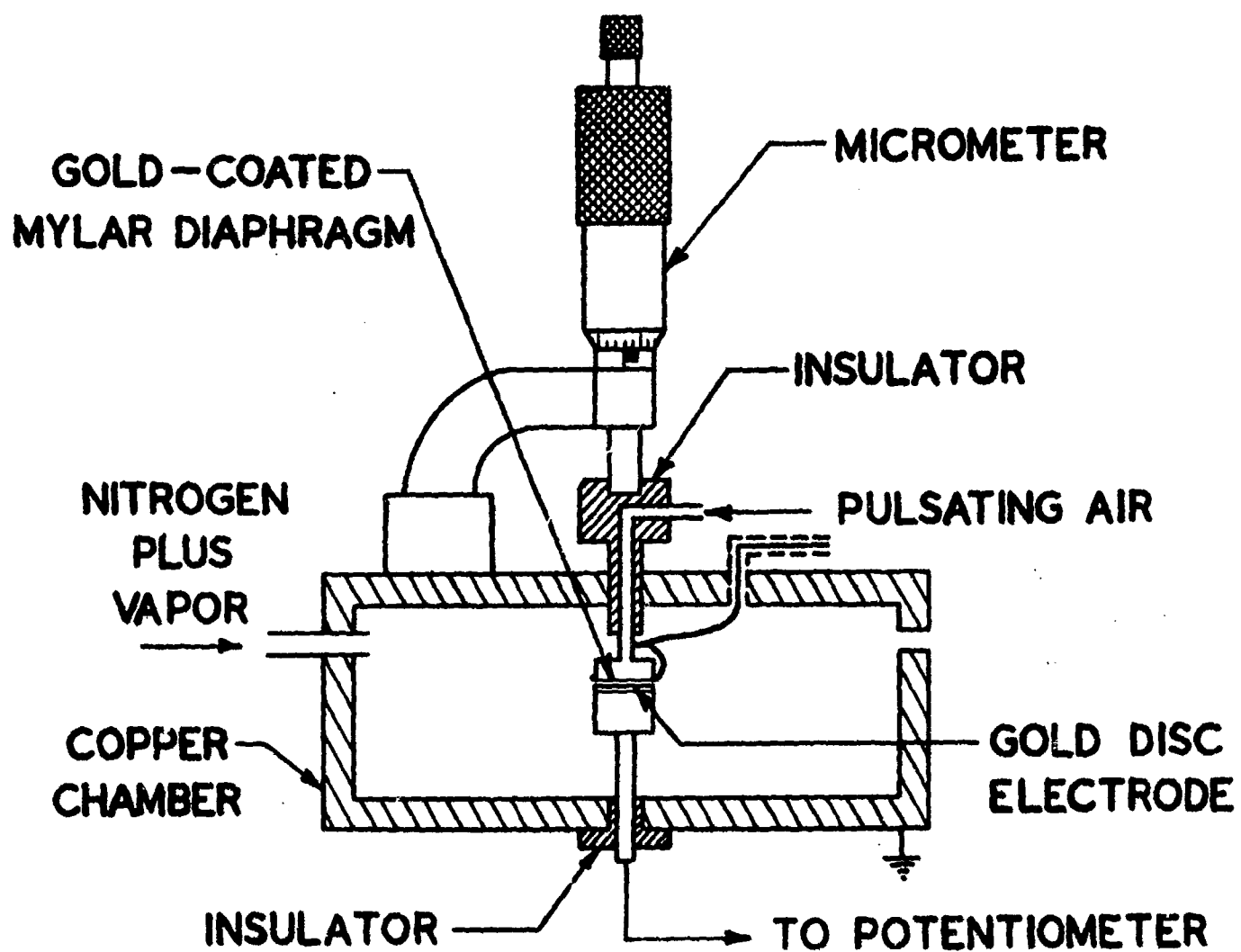


Figure 8

VIBRATING CAPACITOR CHAMBER
FOR CONTACT-POTENTIAL STUDIES

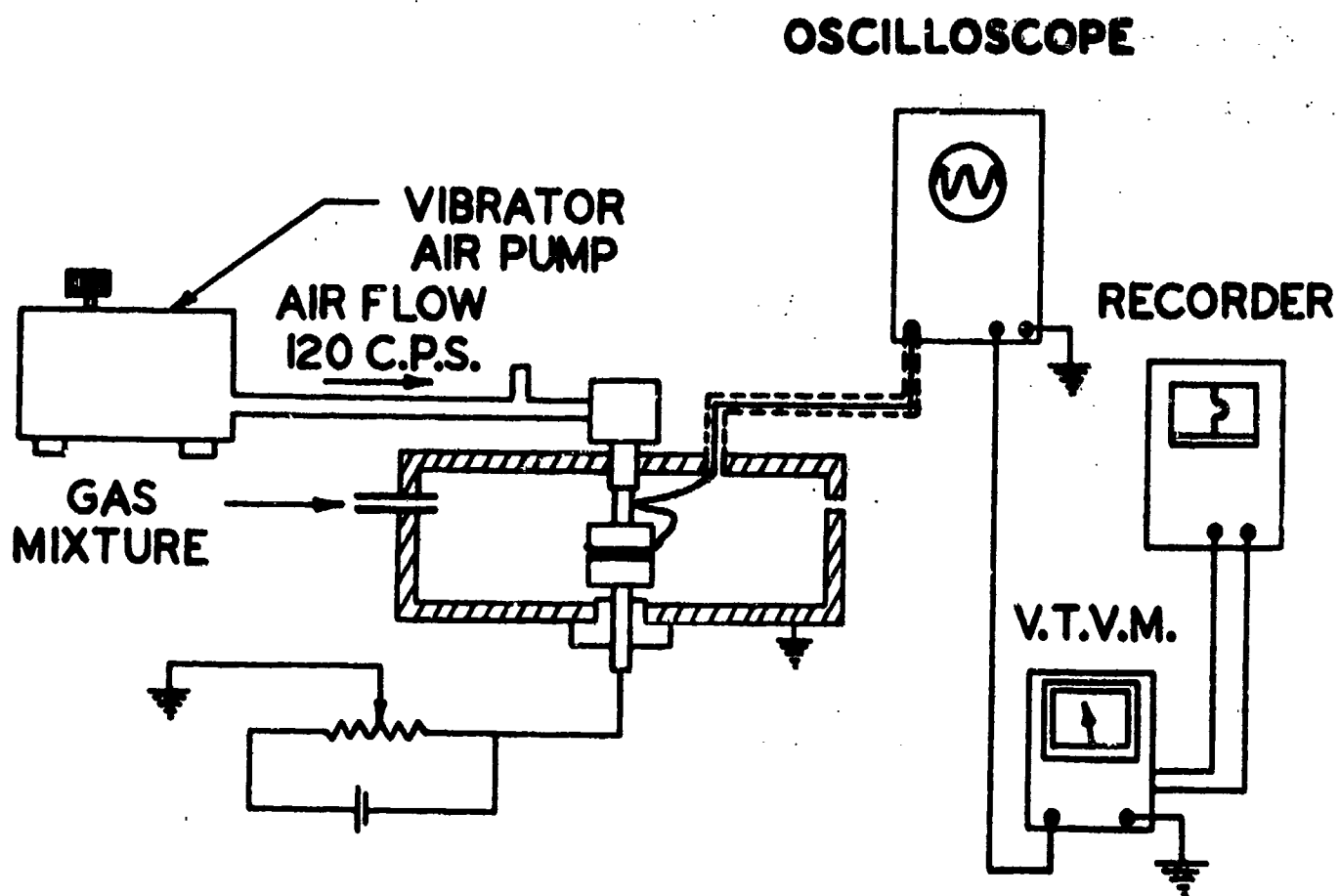


Figure 9
CIRCUIT OF MEASUREMENT AND RECORDING
OF CONTACT POTENTIALS

to the contact-potential apparatus chamber (Fig. 8) at a rate of 40 cm³/min through an aluminum block at 64°C. The contact potential in nitrogen was compared with that in nitrogen with 1.7×10^{14} molecules of DNT per cm³. The DNT-containing stream was generated by introducing the compound into the path of the nitrogen flow in the preheater.

Further experiments were conducted with several sensor substances that are known good electron donors. DNT and nitroglycerin vapors were included in this series. All tests used partial pressures of the vapors of explosives at, or close to, saturation. The objective of the series was to spot suitable sensors; the sensitivity and specificity study to be later. The results are summarized in Table II.

Table II
CHANGES OF CONTACT POTENTIALS
UPON INTRODUCTION OF DNT VAPOR

<u>Sensor Surface</u>	<u>DNT</u>	
	<u>Concentration,</u> <u>molecules/cm³</u>	<u>Contact Potential</u> <u>change, mv</u>
CaSO ₄ ·2H ₂ O	~10 ¹⁴	+17
Graphite	~10 ¹⁴	0
Gold*	~10 ¹⁴	-48, drifting
Gold**	~10 ¹⁴	0
Gold**	2x10 ¹²	-4
Chlorpromazine**	2x10 ¹²	-13
Carotene	2x10 ¹²	-4

*The reference plate was coated with paraffin wax to desensitize it against adsorption.

**The reference plate was coated with Kynar (vinylidene fluoride polymer made by Pennsalt Co.) film.

Graphite powder was placed on gold by rubbing the gold surface with powder until a shiny coat appeared. Chlorpromazine hydrochloride film was deposited by evaporating a drop of solution prepared by dilution of the medicinal Thorazine concentrate

(30 mg/cc) with methanol in a ratio of 1:25. Carotene film was deposited by a similar technique from a solution of 50 mg of carotene in 1 cc of methanol.

In addition, experiments were conducted in which, instead of continuous introduction of the vapor, 10^{-3} g of nitroglycerin was injected in a single package into the nitrogen stream in a preheater (64°C) that was ahead of the contact-potential apparatus chamber. The reference plate in this case was Kynar-coated gold, the sensor bare gold. The rate of nitrogen flow was 180 cm³/min. The observed contact potential increase was +5 mv.

In these experiments only indications of sensitivity of some sensors to the vapors of polynitro compounds were obtained. Much more work will be necessary to advance this technique to a stage from which realistically sensitive and specific sensors will emerge.

2.3.2 Comparison of Contact-Potential and Electron-Capture Techniques

The demonstrated sensitivity of the electron-capture process used in conjunction with gas chromatography is approximately 10^{-10} to 10^{-9} of the polynitro or organic nitrate compound present in the explosives.

The sensitivity of the contact-potential method can be theoretically evaluated from reasonable assumptions. A contact-potential change of 1 mv for a sensor plate with an area of 0.1 cm² is reasonably within the state of art; this accounts for the uncertainties caused by contact-potential drifts common in sensors. We optimistically assume that adsorption and formation of the charge-transfer compound produces a dipole contribution of 2 Debye units in the direction normal to the sensor.

By rearranging Equation 2.2-1 the number of molecules per sq cm needed is

$$n = \frac{\Delta E}{3.77 \times 10^{-15} \cdot \mu_2} = \frac{10^{-3}}{3.77 \times 10^{-15} \times 2} = 10^{11} \quad (2.3.2-1)$$

For the area of 0.1 cm², the number of molecules required will be less, but, on the other hand, some adsorption will also occur on walls and other parts of even a small sensor chamber. Also, the surface of the sensor is unlikely to be perfectly smooth; the true area is several times larger than the geometric area, even for relatively smooth surfaces. On such a basis, the ultimate sensitivity of a charge-transfer effect sensor based on contact-potential can be 10^{11} molecules, or 2×10^{-11} g, for a substance such as nitroglycol with a molecular weight of 152.

Thus, analysis indicates that the extrapolated sensitivity of the contact-potential sensor is perhaps 5 to 10 times better than the present demonstrated sensitivity of the combined gas-chromatographic electron-capture process. Moderate improvements in the latter can easily bring the sensitivity beyond the level of the extrapolated advances for the contact-potential sensor.

On the basis of the orientation experiments and the above theoretical analysis, preference was given to the electron-capture detector process in further work.

3.0 DETECTION OF EXPLOSIVES' VAPORS IN ATMOSPHERES

In real environments in which explosives must be detected, the concentration of the explosive's vapor usually will not reach the level that corresponds to the saturation vapor pressure.

The rate of the emanation of vapor from an explosive depends on the rate at which the volatile molecules diffuse from the explosive to the bulk of air. For a pure compound in air, the emanation rate from Fick's diffusion law is approximately

$$J_a = A D_a \frac{n_s - n_a}{x_a} \quad (3.0-1)$$

where J_a is the mass flow from the surface in molecules of vapor per second; A is the geometric surface area of the explosive, cm^2 ; D_a is the diffusion coefficient for the vapor of explosive in air, approximately $0.1 \text{ cm}^2 \text{sec}^{-1}$; n_s is the concentration of the explosive's vapor in molecules per cm^3 within molecular distance from the surface and is usually equated to the concentration at saturation; n_a is the concentration in the bulk of air in which convective air currents take over the dissipation of the vapor; and x is the formal thickness of the nonturbulent boundary layer of air.

The value of x depends on the intensity of air flow and turbulence at the explosive. For natural convection in the absence of induced air currents or drafts, x is on the order of 0.1 to 0.2 cm.

The value of n_s is lower for a complex explosive as compared to the pure substance. Emanation of the more volatile molecules, e.g., DNT in TNT, from the surface depletes the concentration of DNT in the surface. New molecules can arrive at the surface by diffusion from the bulk of the explosive, trying to restore the equilibrium distribution. Hence in a complex explosive when the environment is not saturated with DNT, the effective value of n_s may be lower

*More exactly, the rate of vaporization also depends on the accommodation coefficient of molecules at the surface for substances from which every surface molecule with adequate energy can equally easily evaporate; this coefficient is unity. For some substances, only a fraction of surface molecules possessing adequate energy are able to leave the surface, e.g., only those in some particular orientation. Thus for iodine at 0°C the accommodation coefficient is 0.01, and the rate of vaporization will be correspondingly slower.

than the equilibrium n_s ; the difference depends in a complex way on J , the diffusion coefficient of DNT in the explosive, and the length of time allowed for the emanation. When the complex explosive is in a granulated form, diffusion of DNT from deeper-placed grains can also occur through the space between the grains, and n_s may remain closer to the equilibrium saturation value.

When the explosive is wrapped, e.g., dynamite in wax paper, or in a plastic film, a third diffusion step is added, since now the mass transport through the paper must occur before the volatile molecules can begin to diffuse through the nonturbulent air film.

$$J_p = A D_p \frac{n_s - n_p}{x_p} \quad (3.0-2)$$

Here, D_p ($\ll D$) is the diffusion coefficient through paper or plastic; n_p is the concentration of the explosive's molecules in air at a molecular distance from the paper or plastic film; and x_p is the thickness of this film. Here, the flux J_p is in series with J_a , which is now

$$J_a = A D_a \frac{n_p - n_a}{x_a} \quad (3.0-3)$$

When the diffusion and turbulence stabilize, $J_p \approx J_a$. Any hole or incomplete wrap complicates the conditions further, since then the parameters in the above equations differ for different surface areas.

The value of n_a , the concentration of the explosive's molecules in the air at a distance of a few mm from the explosive, begins with $n_a = 0$ and gradually increases with time. In a closed small environment with poorly sorbing walls, n_a eventually reaches the value of n_s , and the emanation ceases, i.e., the rate of vaporization becomes equal to the rate of condensation of vaporized molecules back unto the surface.

Most of the natural environments are, however, only partially closed, or nominally closed, but the walls are leaky, porous, or sorbent. Various articles that can be present adsorb or dissolve the vapors of the explosive in themselves. Leakage, sorption, etc. act to decrease n_a . As long as n_s or n_p is considerably larger than n_a , small changes in n_a have little influence on the concentration difference term. Therefore, in the first approximation, $n_a = 0$; in detection in leaky or sorbent environments the rates of emanation can be

considered approximately independent of the concentration measured at some distance from the explosive.

At the observation or sampling point at a distance from the explosive, the local concentration of the explosive's vapor depends on the dynamic equilibrium between the emanation from the explosive and the processes that remove the vapor. For a point in the air in a suitcase, the vapor removal process can consist of leakage from a suitcase to the aircraft cabin through a lock or the space between closing edges, diffusion to cabin air through pores in the suitcase walls or through the polymeric materials of the wall, and sorption in paper, fabrics, leather, and other materials in the suitcase.

For a sampling zone outside of a suitcase, even if this zone fully surrounds the suitcase, only those molecules that were emanated but did not absorb or adsorb in the suitcase are available. Since the vapor continues to dissipate beyond this zone, the steady-state concentration at a sampling point in the zone is again determined by the dynamic equilibrium between the rates of arrival and dissipation.

This discussion has indicated the complexity of factors that together determine the concentration of the explosive's molecules in the air at some sampling point. Although the overall relations are clear, in most cases the parameters that are needed to calculate the expected concentrations are not available; diffusion coefficients and rates of sorption of nitroglycol and DNT in various common materials, the leakages through packaging materials, luggage walls, etc., are unknown.

The shortest route to obtaining the estimates on the concentration of explosive's emanated molecules in various environments is therefore through empirical measurements in a few typical situations. Experiments on the rates of accumulation of vapors in several environments and on their final concentration are described in subsequent sections.

3.1 Experimental Technique

The flow method for collecting vapors and measuring volumes is effective in determining vapor pressures but is a specialized technique that cannot be applied in a simple form to the problem of bomb detection on passengers and in luggage or other cargo. It is also clear that the detection of vapors in a gas sample on a "yes" or "no" basis is simpler than measuring the exact vapor pressure of a material.

It was soon found that all the explosives on hand (except ammonium nitrate) could be detected by a syringe sampling of the air above them when they were stored in glass jars, cardboard boxes, and other containers. Approximately 3.0 cc of air was all that was necessary to detect the presence of explosive vapors in these favorable geometries, and a series of experiments was planned around the simple syringe-sampling technique.

3.2 Hermetic Containers

Materials with relatively high vapor pressures come to steady dynamic equilibrium with their surroundings more rapidly than lower vapor pressure materials. Therefore, we initially chose to study dynamites containing nitroglycol, which has a relatively high vapor pressure.

In Figure 10 the rate of buildup of nitroglycol vapor in a 2-gallon glass desiccator is charted. The saturation of the air in the closed volume was quite rapid; it reached 75% of its final value in less than 20 min. A $\frac{1}{4}$ -lb stick of Gelamite-1 commercial explosive was the source of the nitroglycol in this case.

Further experiments were conducted with other explosives in 1-gallon glass jars with screw tops. Nitroglycol and nitroglycerin were detected with the syringe method above the 40-mm smokeless powder. DNT and TNT were detected above Vibronite B, Composition B, and the nominally pure TNT. In all cases, saturation vapor concentrations were approached within an hour or less.

3.3 Leaky Containers

Another set of experiments is illustrated in Figures 11 and 12. In Figure 11 a beaker containing a few grains of Gelobel-C was placed in a cardboard box for $3\frac{1}{4}$ hr and then removed. The variation in nitroglycol concentration with time was measured. There is an initial rapid rise and fall in the concentration due possibly to a sampling peculiarity, but the concentration soon began to increase steadily, as in the desiccator experiment above.

After the Gelobel-C was removed, the nitroglycol concentration fell rapidly at first but lingered at an easily measurable level until the next day.

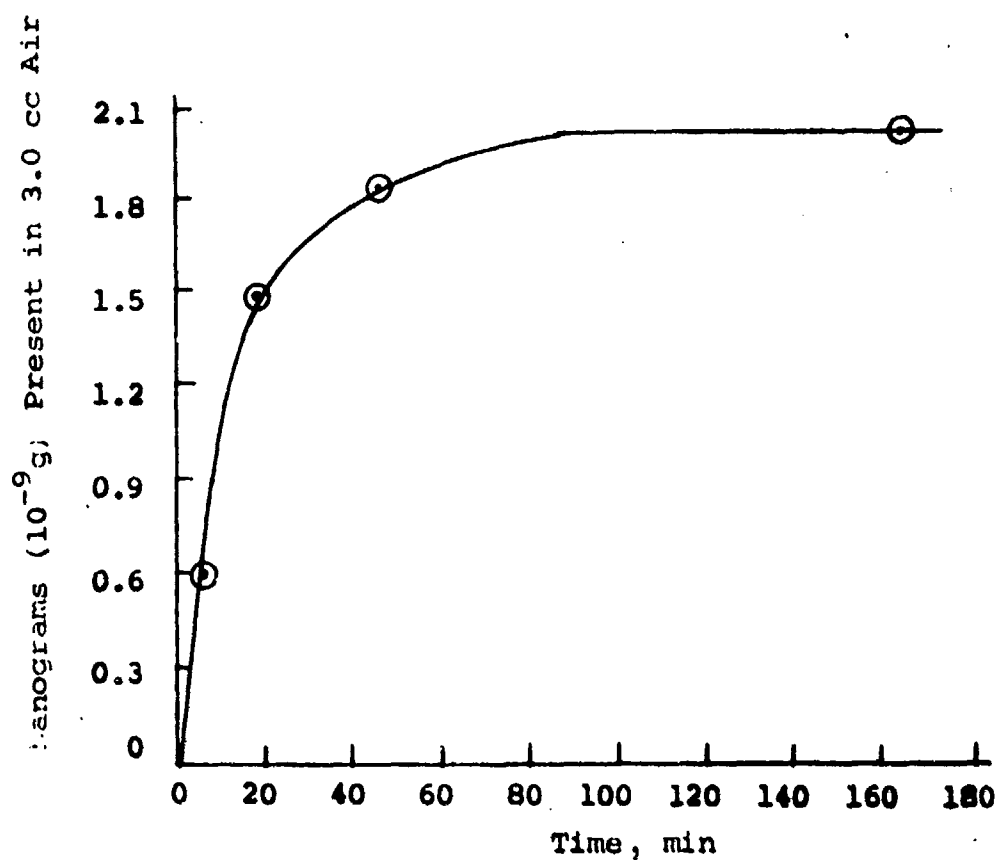


Figure 10

BUILDUP OF NITROGLYCOL FROM GELAMITE-2
COMMERICAL 1/2-LB DYNAMITE STICK IN A GLASS DESICCATOR

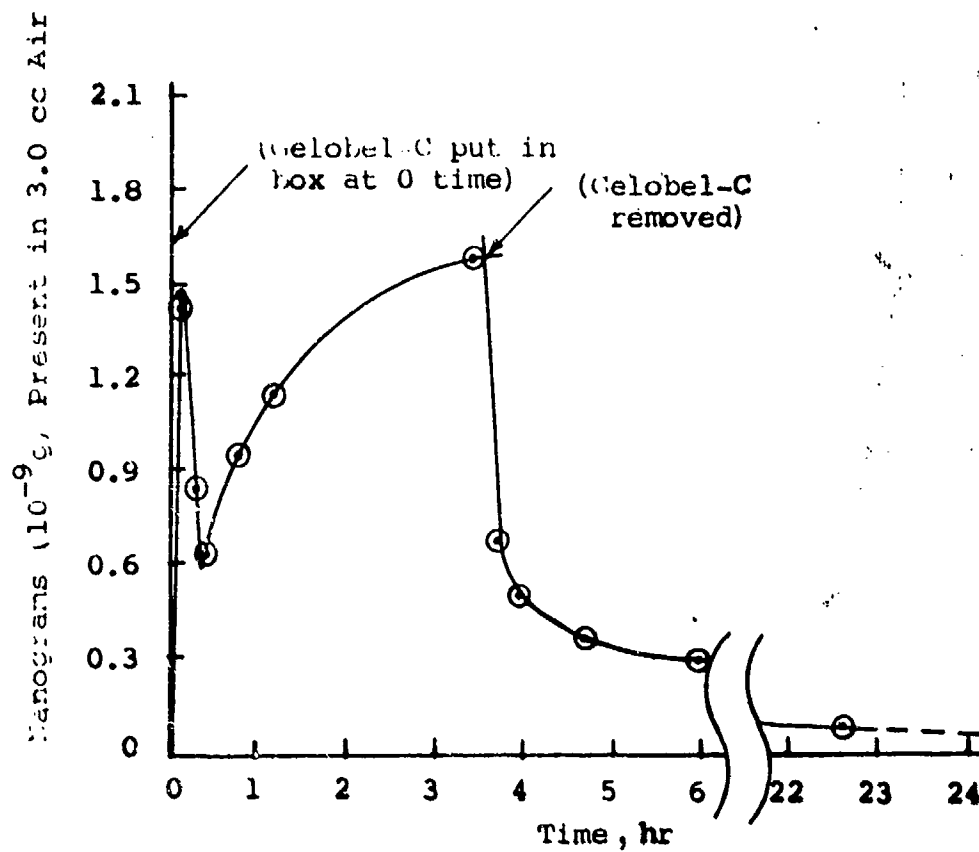


Figure 11
BUILDUP AND DECAY OF NITROGLYCOL
FROM GELOBEL-C IN A CARDBOARD BOX

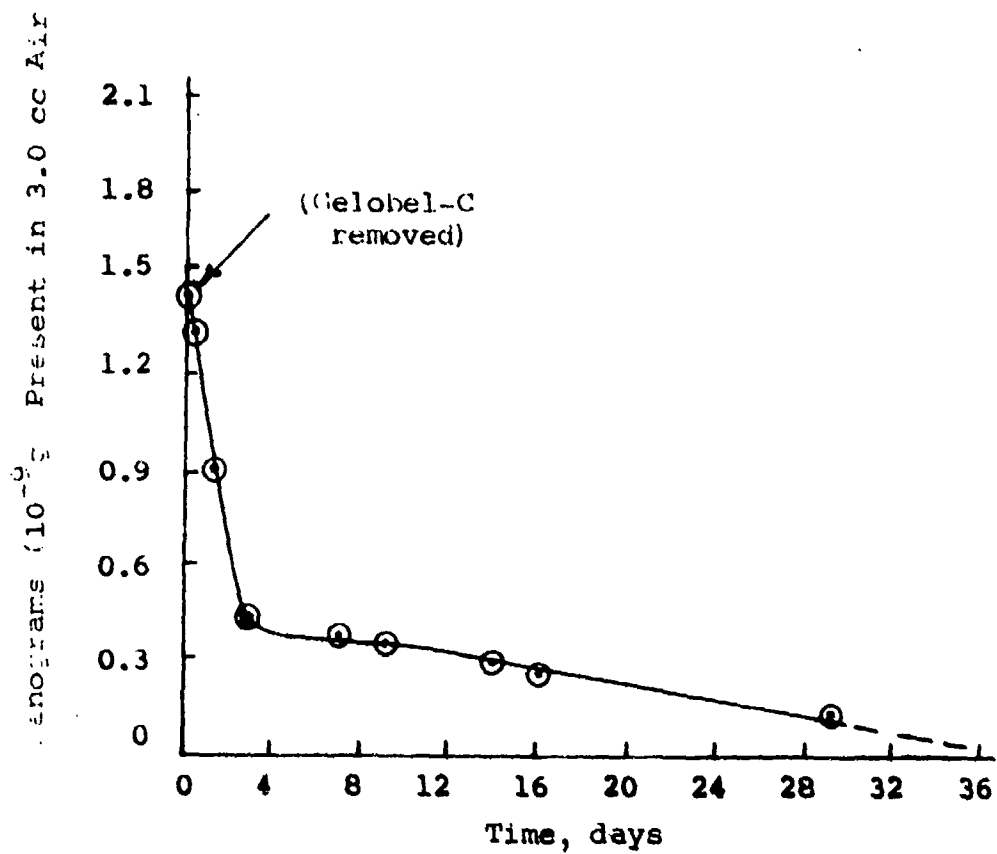


Figure 12
NITROGLYCOL REMAINING IN THE VAPOR IN A CARDBOARD BOX
AFTER REMOVAL OF GELOBEL-C DYNAMITE
(THE GELOBEL-C WAS IN THE BOX 1 WEEK)

In a similar experiment another box was used to store Gelobel-C vapors for one week. The source was then removed and the nitroglycol concentration measured over a period of 29 days. As can be seen in Figure 12, measurable amounts of nitroglycol still remained after 29 days of standing empty in still air.

Note that only 3.0 cc of air was removed from the box or desiccator in each measurement, and no preconcentration of the vapors was necessary. Obviously, larger air samples and preconcentrations will allow much lower concentrations to be measured.

Experiments with suitcases in which dynamite was placed together with other articles and substances that produced irrelevant vapors are discussed in Section 4.3.

3.4 Retention of Vapors at Surfaces

As was evident from lingering of the nitroglycol vapors in containers after removal of the explosive, nitroglycol tends to adsorb strongly at surfaces. Additional tests were conducted on retention of nitroglycol at glass and metal surfaces.

Figures 13 and 14 illustrate, respectively, how nitroglycol vapors lingered on our $\frac{1}{4}$ -cc sample syringe with the time and through several acetone rinsings. Thus, the sampling procedures must be carried out very carefully to ensure that the sampling devices are not contaminated from earlier tests.

3.5 Detection in Open Air

In the experiments discussed above, the concentration of the nitroglycol or DNT vapors was sufficient for sampling with a 3-cm³ syringe. For more difficult detection tasks at lower concentrations, a larger air sample must be sampled. This was accomplished by pulling air through a capillary sampler.

The sampler is a stainless steel tube 17 in. long, 1/16 in. OD, and 1/32 in. ID. Air is pulled through at room temperature by connecting one end of the capillary to Dyna-Vac pump (Cole-Parmer Instrument Company). Approximately 300 cm³ of air/min could be passed through the sampler. Nitroglycol is adsorbed by the stainless steel surface (Section 4.3). After a sufficient length of sampling, the capillary is placed in the carrier gas stream ahead of the injection port of the gas chromatograph. The capillary is flash-heated by passage of electric current by using the capillary as the heating element. Nitroglycol desorbs from the inner surface of the capillary and is processed by the gas chromatograph as usual.

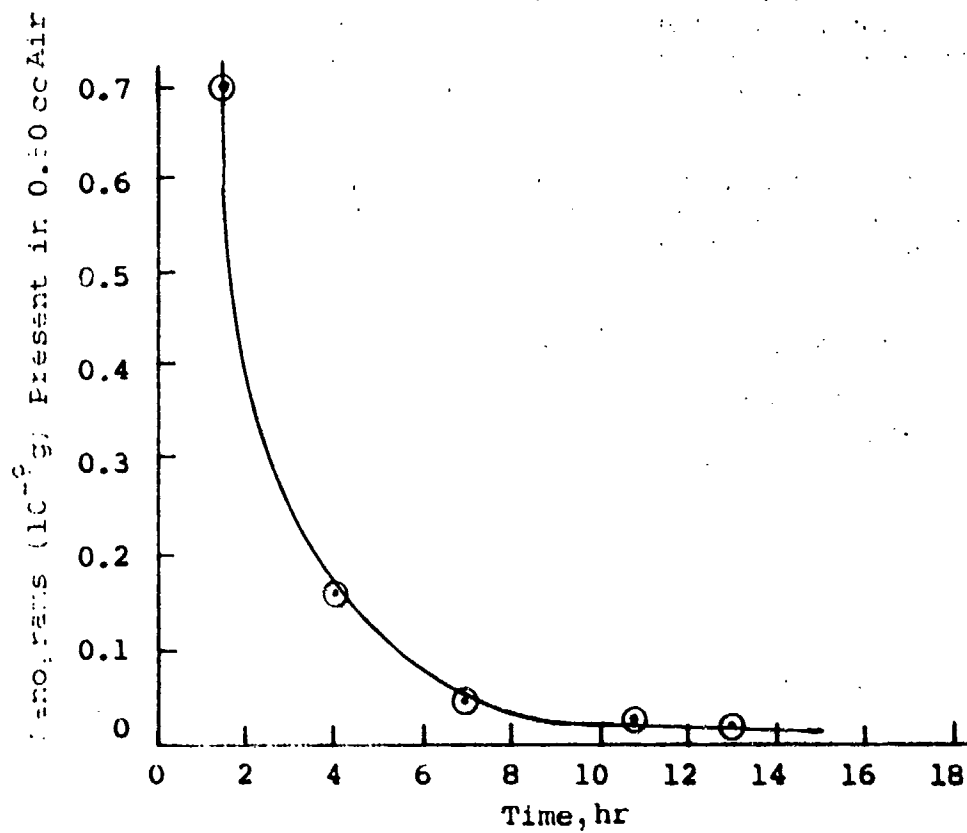


Figure 13

NITROGLYCOL REMAINING IN A 0.50-CC SYRINGE
AFTER LYING OPEN FOR A NUMBER OF HOURS

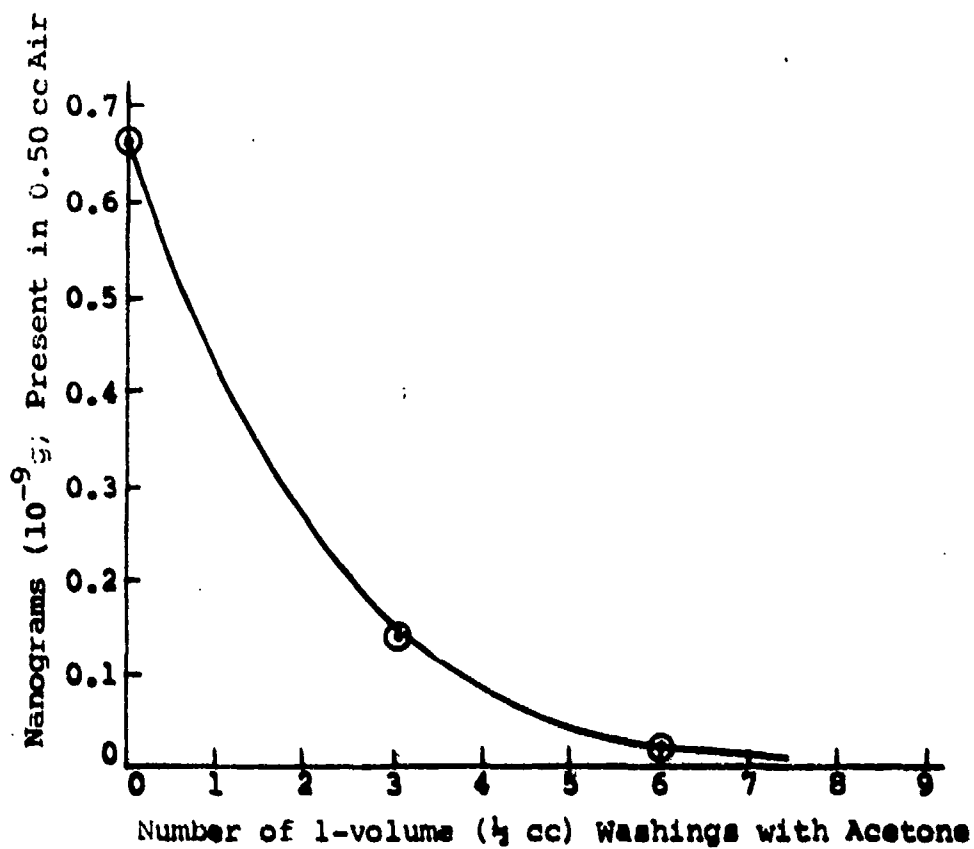


Figure 14

NITROGLYCEROL REMAINING IN THE VAPOR
IN A 0.50-CC SYRINGE AFTER REPEATED ACETONE WASHINGS

With this arrangement, air was sampled at various distances from a stick of dynamite placed openly on a table top at its edge in a well-ventilated laboratory. Smoke was used to estimate the air movements in the room. The air moved in a preferred direction at approximately 10 ft/min with superimposed turbulence. At a distance of 6 in. from the dynamite, 1-liter and 5-liter samples of air were taken, and 3.5×10^{-10} and 5×10^{-10} g were recovered from these. At 3 ft, the nitroglycol concentration level was below the detection limit of this primitive technique.

We believe that the efficiency of flashing was low; we have not yet established (1) what levels of flashing temperature can be tolerated by the thermally unstable nitroglycol vapor at various lengths of the capillaries, (2) which metals or other materials are less catalytic in decompositions of nitroglycol, and (3) how long the capillary must be to adsorb most of the vapor.

Experiments were also conducted to detect nitroglycol on the skin of palms of hands or on the surface of a glass jar handled by a person after handling a stick of dynamite. The detection technique was not yet sufficiently sensitive to give definite positive results in conjunction with the simple form of sampling used. At best, faint distortions in the appropriate position in the gas chromatograph were observed.

The technique must be developed further if it is to accomplish the task of detecting of an explosive's vapors adsorbed or absorbed by objects or skin.

4.0 DETECTION OF EXPLOSIVE VAPORS IN PRESENCE OF IRRELEVANT AIR CONTAMINANTS

The experiments described above demonstrate the feasibility of vapor detection of explosives but use more or less idealized laboratory situations. In a bomb detection system the explosive vapors will have to be detected in the presence of countless other types of molecules, which may mask the substances sought and give false signals or otherwise upset the detection system.

4.1 Vapors Emanating from Common Objects

A series of experiments to test the effects of everyday objects on explosive vapor detection was carried out. Items that would appear in luggage and purses were mainly selected. Such things as perfumes, shoe polish, shaving cream, and other

items for personal care may not be in the bomb-containing luggage or cargo box but would be in other innocent containers from which air would also be sampled.

4.1.1 Sampling Equipment and Procedures

A 9-liter desiccator containing the explosive was allowed to equilibrate, usually overnight. The desiccator was then attached through a cold trap to a water aspirator, and a vacuum of 150 mm Hg was drawn. This is equivalent to removal of approximately 20% of the atmosphere of the desiccator, or 1.8 liters.

A U-shaped glass tube (4 mm ID) immersed in a dry ice-acetone bath served as the trap for the vapor component.* Benzene (1 cc) was used to wash out the trapped materials. Benzene was selected here as the solvent to effect a separation of a large amount of water collected from the desiccator air in the dry ice-cooled trap. This water problem, important in large-volume sampling, is discussed in Section 4.3. An aliquot of the benzene solution was analyzed on an Aerograph model 350A gas chromatograph equipped with an electron-capture detector. The column was 18 ft x 1/8 in. copper, and the walls were coated with Carbowax 4000. The operating temperatures were 80°C for EGDN detection and 110°C for DNT detection.

4.1.2 Experiments

The series of experiments shown in Table III was performed. Each was set up in the 9-liter desiccator and sampled as previously described. A series of blanks were sampled without the explosives (Exp. 1 through 5).

A standard solution of nitroglycol (ethyleneglycol dinitrate, EGDN) was obtained from Dr. Lawrence of Hercules Powder Company. It contained 0.0114 g/ml nitroglycol. This was diluted by a factor of 400 to get a working solution of 28.5×10^{-9} g/microliter, 1 microliter of which gives a peak of 8.9 chart units at a retention time of 30 sec. This is identical to that of the vapor from Gelamite and 40-mm gun powder.

DNT solutions were prepared from pure 2,4-dinitrotoluene. One microliter contained 12.7×10^{-9} g and gave a peak of 9.5 chart units. The retention time was 1.25 minutes, the same as that observed in vapor from Vibronite and Composition B explosives.

* See Appendix for a photograph of laboratory equipment.

Table III
EXPERIMENTS ON COMMON OBJECTS

<u>Exp. No.</u>	<u>Explosive Present</u>	<u>Other Objects Present</u>
1	None	Super insect bomb
2	None	Shoe polish
3	None	Shaving cream
4	None	Hairspray
5	None	1 cc jet fuel; tooth- paste, shaving cream, and shoe polish
6	Gelamite	None
7	Gunpowder	None
8	Composition B	None
9	Vibronite	None
10	Gelamite-1	Contents of a lady's purse
11	Gelamite-2	Gillette shaving cream, Shinola black shoe polish, Crest tooth- paste
12	Gelamite-3	1 cc jet fuel (JP5) on filter paper
13	Gunpowder-1	Shoes and gloves
14	Composition B-1	Labcoat
15	Vibronite-1	Playing cards, sun- glasses, plastic rain- hat, cigar

4.1.3 Results

The results of these experiments are presented in Table IV. The shoe polish and hairspray contain materials that give large responses on the electron-capture detector (Exps. 2, 4, and 5). However, they come out slightly sooner than the nitroglycol and much sooner than the DNT.

The column-labelled quantity of vapor collected is that collected at the indicated retention time. Experiments 6a through 6d on Gelamite alone indicate the reproducibility of the technique. Experiment 7 shows that the gunpowder is about half as strong a source of nitroglycol as the Gelamite. Apparently this same ratio holds for Vibronite and Composition B as seen in Exps. 8 and 9.

In experiment 10 an old leather woman's purse containing perfume, lipstick, keys, a small handkerchief, etc. was placed in the desiccator. These items seem to have reduced the vapor concentration by about 1/2. In experiment 11 the apparent amount of Gelamite vapor is almost twice that in 6a through 6d. This is due to overlap of the shoe polish peak and the nitroglycol. This problem can be eliminated by using a longer column and a somewhat longer retention time.

In experiment 12, Gelamite and 1 cc of JP5 (jet fuel on a piece of filter paper) were placed in the desiccator. The amount of nitroglycol is reduced compared with experiment 6, but no other peaks were observed, showing the electron-capture detector to be very insensitive to the saturated hydrocarbons in JP5 vapor.

In experiment 13 the nitroglycol peak was cut in about half due to absorption on shoes and clothes, and in experiment 14 a large labcoat placed on top of Composition B in large chunks reduced the vapors below the limit of detection, which is about 1×10^{-9} g in these experiments.

4.2 Contaminants in Airport Air

An additional series of experiments was performed at O'Hare Airport in the facilities of United Air Lines by taking air samples in gas bulbs as follows:

Table IV

VAPOR COLLECTED FROM COMMON OBJECTS
IN THE PRESENCE OF EXPLOSIVES

Exp. No.	Description	Retention Time, sec	Quantity of Vapor Collected, micrograms
1	Insect bomb	n.a.	0.003
2	Shoe polish	15	2745
3	Shaving cream	n.a.	0.003
4	Hairspray	10	61
5	Shoe polish, etc.	20	1022
6a	Gelamite alone	30	190
6b	Gelamite alone	30	261
6c	Gelamite alone	30	224
6d	Gelamite alone	30	265
7	Gunpowder alone	30	118
8	Composition B alone	75	10.7
9	Vibronite alone	75	5.1
10	Gelamite + purse	30	131
11	Gelamite + shaving cream, shoe polish, and toothpaste	30	549
12	Gelamite + JP5 (jet fuel)	30	141
13	Gunpowder + clothes	30	61
14	Composition B + Labcoat	75	0.001
15	Vibronite + glasses, cards, cigar, rainhat	75	0.81

Note: n.a. - not applicable, nothing collected.

(1) Plane being loaded, at plane	1 liter
(2) Jet taking off, behind the plane	2 liters
(3) Passenger lounge	250 ml
(4) Loading ramp, boarding outlet	250 ml
(5) Baggage room	125 ml
(6) Main lobby	125 ml

Aliquots (3 cc) of the air samples were run on a hydrogen-flame detector. The samples showed trace quantities of hydrocarbons, presumably from jet fuel vapor. The remainder of the air samples were pumped into a trap by means of a water aspirator, washed out of the trap with 1 cc of benzene, and analyzed with the electron-capture detector.

All the samples showed trace amounts of some material not believed to result in interference with detection of nitroglycol (EGDN). The largest amount of the unknown material was found in the baggage room.

The authors wish to acknowledge the help of Mr. Robert Carlson of United Air Lines in gaining access to the facilities mentioned above and in escorting us around the Airport.

4.3 Analysis of Sampling Processes

As indicated in Section 4.1, sampling procedures that use refrigerants, such as dry ice-acetone mixtures and liquid nitrogen, remove all condensible components from the air. The problem of water vapor is most important, since at room temperature and a relative humidity of 50% it represents 1.6% of the volume of the air, or about 12 mg/liter. The detection of 10^{-9} g quantities of an explosive's vapor in samples of 100 to 1000 liters of air would involve collecting along with this small quantity up to several cubic centimeters of water. The explosive would then have to be separated from this large volume of water, thus necessitating an additional step and complicating the detection process.

In any bomb-detecting scheme, a positive identification of an explosive vapor is all that is required. The actual concentration of the vapor is relevant only to the minimum amount of material needed for identification. Also, in the use of the electron-capture detector, the passage of large amounts of anything other than the carrier gas can adversely affect its sensitivity and interfere with the detection. Therefore, a more selective, although possibly somewhat less efficient, collection process was sought.

4.3.1 Separation by Physical Adsorption

As noted in Section 3.4, nitroglycol vapor clings to the walls of the syringe tube and needle for hours after it has been exposed to nitroglycol-containing sample. The process by which the molecules linger on the tube surface is called adsorption in order to distinguish it from the bulk effect of absorption (Section 4.3.2).

Later it was found that the tiny needle of a 10-microliter syringe would retain much more nitroglycol than could be accounted for by the vapor pressure of the nitroglycol and the volume of the syringe. Hence, the nitroglycol molecules were being adsorbed on the needle walls and desorbed (evaporated) after the needle had been inserted into the heated metal block of the chromatograph.

On the basis of the length and volume of the needle tube, the internal surface area is estimated to be about 0.310 cm^2 . From the molecular weight and density of nitroglycol the surface area of a single molecule can be estimated as 29 \AA^2 . Thus 0.31 cm^2 will hold 1.07×10^{14} molecules or $27 \times 10^{-9} \text{ g}$ in a monolayer. Such layers can readily form at 5 to 10% of the saturation vapor pressure observed in the jar experiments.

The technique of collection by adsorption on a tube wall has many of the desired characteristics of an ideal sampling procedure. Since the surface area is limited, only a small amount of material can be retained, thereby automatically limiting the amount injected into the detector. The method is selective because low-vapor-pressure polar materials, such as nitroglycol, adsorb more strongly than smaller water molecules and displace water from the surface.

During the experiments described in Section 3.5 the detection of nitroglycol by the capillary-tube method had limited success. The problem seems to be the decomposition of the nitroglycol on the tube surface before it is inserted in the chromatograph. This is caused by the catalytic action of metals on unstable organic molecules and is a limitation of the use of metal surfaces as adsorbents. It should be possible to overcome this problem by using a more inert metal or by using the separation scheme described below.

4.3.2 Separation by Bulk Absorption

Another separation scheme would involve absorbing the explosive molecules in a thin film of grease or oil on the surface of a tube or bundle of tubes. These tubes would then be heated to evaporate the vapors into the chromatograph. The tubes could be made of glass or Teflon* plastic to provide an inert noncatalytic surface.

* Du Pont Co. polyfluoroethylene plastic.

To enhance the trapping effect of the thin grease film, electron donor compounds, which form loose complexes with polynitro compounds, could be incorporated in it. Such compounds are described in Section 2.1.

To summarize, in addition to lower-temperature trapping, a number of processes which are available will greatly enhance the selectivity and sensitivity of the sample-collection procedure. Further development and testing beyond that accomplished in this work are required. Proper sample collection process can greatly assist in elimination of interferences from major air contaminants.

5.0 DETECTION THROUGH MICROWAVE ABSORPTION

During the program, the possibility that nitroglycol vapor could be detected through microwave absorption was explored as an additional detection principle. This effect is finding increasing use in the study of the molecular properties of polar molecules* in vapor form.

When an electromagnetic wave with a sufficiently low frequency acts upon a polar molecule, the oscillating electrical field induces the rotation of the molecular dipole. The rotational energy can be accepted by the molecule only in discrete quantities, ΔE , depending on the momentum of inertia of the molecule around the axis of its rotation. For a simple molecule with one momentum of inertia:

$$\Delta E = \frac{h^2}{8\pi^2} \frac{J(J+1)}{I} \quad (5.0-1)$$

where h is Planck's constant, I is the appropriate momentum of inertia, and J is any integer. The value of the rotational quantum, ΔE , is connected to the frequency of the impinging electromagnetic wave through

$$\nu = \frac{\Delta E}{h} \quad (5.0-2)$$

Thus, the energy of the microwave is absorbed by the molecule only if certain characteristic values of frequency are used. Also, a sufficient number of intermolecular collisions must occur between the molecules in the vapor, so that the rotationally excited molecules can lose their energy and be prepared for repeated absorption of the energy from the microwave. Usually the most desirable pressure in the microwave cell is 1 to 100 microns of Hg.

The characteristic absorption frequencies in the microwave range thus describe principally the property of the polar molecule as a whole. This contrasts to the infrared absorption and Raman scattering, which characterize principally the

* Polar molecules are those in which the center of all negative charges (electrons) does not coincide with the center of all positive charges (atomic nuclei), but there is no overall net charge: e.g., in water the configuration is $\text{H}-\text{O}-\text{H}$ and the negative charges are located in the vicinity of oxygen, but the positive charges are closer to the line drawn from H to H.

properties of parts of molecules (bonds, functional groups), and visible and ultraviolet spectra that describe the electronic transitions within the molecule. Microwave absorption peaks are sharp, and the possibility of the coincidence of having almost the same absorption frequencies is very small, and high resolution is instrumentally possible. Small polar molecules consisting of a few atoms have the characteristic microwave frequencies in the 10^{10} to 11^{11} cps range. Smaller molecules, e.g., water, absorb at high frequencies outside of the above range. Large polyatomic molecules absorb at lower frequencies.

Recently, the first commercial version of microwave absorption spectrometer for the range of 820 to 1240 mc has become available.*

Discussions with IITRI personnel competent in rotational spectra and molecular structures established that from existing knowledge about nitroglycol and DNT structures it is possible to predict if microwave absorption occurs in this range.

Accordingly, arrangements were made to determine whether dynamite and DNT samples emanate characteristic vapors that can absorb at some frequency in the above range. Samples were tested in the Hewlett-Packard model 8400 A microwave spectrometer cell equipped with a Stark effect splitter. The latter superimposes a 10^5 electrical field and, by providing some restoring force on the orientation of the molecular dipoles, splits the microwave peak in subpeaks in the vicinity of the absorption frequency.

The testing was conducted in part during the Western Spectroscopy Conference in the instrument set up for the exhibition and later by Hewlett-Packard personnel in their laboratories. The full cooperation of Mr. Stuart Armstrong and his associates of the Hewlett-Packard Company is gratefully acknowledged.

Some peaks observed initially were not confirmed by subsequent tests and were tentatively attributed to artifacts in the circuit and to accidental contamination.

The more reliable results were obtained after careful purification of the absorption cell and freeze-distillation of the dynamite (Columbite-1) sample. Cross-checks with subsequently evacuated cells indicated that the explosive releases vapors that produce microwave absorption peaks at 8500 mc. The pertinent section of the microwave spectrogram is reproduced in Figure 15.

* Hewlett-Packard Company, model 8400 A.

Absorption Intensity

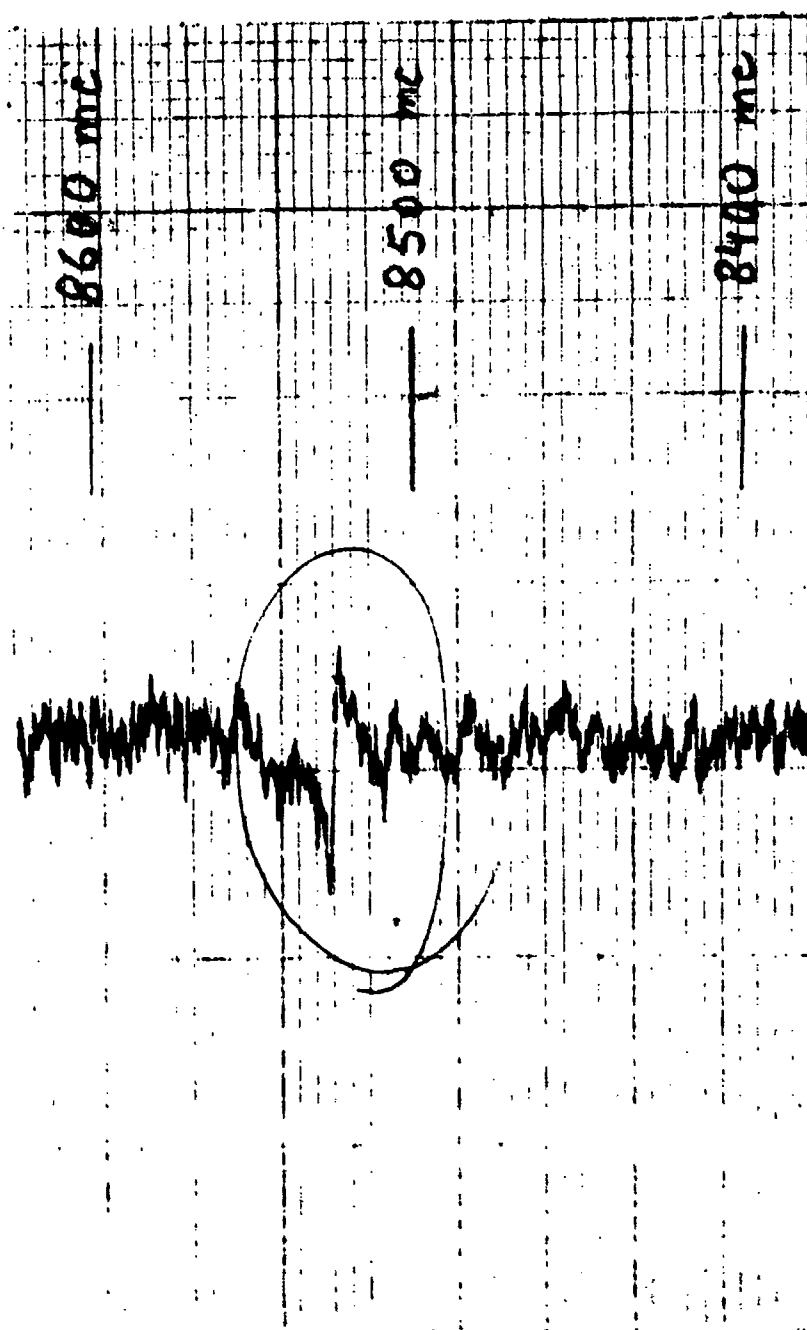


Figure 15

MICROWAVE ABSORPTION PEAK OF GELANITE-1 VAPOR
(COURTESY OF HEWLETT PACKARD COMPANY)

During this test, the pressure in the cell was 200 microns. The partial pressure of the absorption-producing component and its chemical identity could not be established in this short investigation. No reliable information was obtained from the DNT sample.

Thus, the few exploratory experiments on microwave techniques for the detection of dynamite's vapor yielded a positive indication. More experimentation would be needed to confirm these findings and extend the experiments to DNT.

The microwave technique offers positive identification of the chemical species. After the exact position of the peak has been determined, simpler circuitry specializing on this specific frequency can be used and low-level signals distinguished. The microwave absorption varies with the partial pressures of the polar component and other gases present. With a decrease in concentration and total partial pressure, the peak narrows and finally disappears by becoming too narrow. At higher partial pressures, the molecules undergo Stark effect-splitting in the electrostatic field produced by other molecules, and the peaks broaden diffusely. For an optimum detection, the pressure in the absorption cell has to be kept within a certain range. All these factors should be investigated if the study of the microwave absorption detector is continued.

6.0 ANALYSIS OF IMPLEMENTATION OF THE BOMB DETECTION SYSTEM

On the basis of the information and experimental data obtained in this work, the feasibility of systems for bomb detection through chemosensing means can be analyzed.

In the proposed bomb detection technique, characteristic vapors emanated by explosives are detected instrumentally. Among the characteristic vapors, nitroglycol and dinitrotoluene are the most useful, since one or both of these substances are encountered in most explosives. Thus, the presence of vapors of either indicates high probability that an explosive is present. A bomb that contains homemade explosives as its major portion will be either too bulky (black powder) or will require an initiation booster, which most likely will contain either nitroglycol or DNT. The availability of explosives not chemically susceptible to detection by analysis for nitroglycol or DNT is low. All bombings up to date have utilized dynamites (ref. 1) that in principle can be detected as far as the nature of their vapors is concerned.

Some irrelevant materials have been found (Section 4) that interfere with detection of nitroglycol when the technique is used in its present early stage of development. The vast majority of common irrelevant materials do not interfere, since two requirements must be met by an interfering chemical species: (1) its partition coefficient for the gas-Carbowax 20 system at a certain temperature must be the same as that for the nitroglycol and (2) it must have a strong affinity toward electrons. The temperature level is interrelated with the volatility of the compound; in the temperature range used in the present work in the gas-chromatographic column, only relatively small molecules have sufficient vapor pressures. Thus, although the number of chemical species that are volatile enough is large, it is still limited; only molecules with sufficient polarity will have similar partition coefficients, and only a fraction of these can be sensed by the electron-capture detector. Although additional interfering substances might be found in further studies, not many of these can be expected. Modifications to deal with the interferences are feasible in the detection technique and no unsurmountable difficulties are expected in this direction.

Consequently, the prospects for an implementation of the bomb detection method are good as far as the specificity and the ability to deal with irrelevant air contaminants are concerned.

Other major questions in the implementation analysis concern the location and speed of the detection process, the prospects for attaining sufficient sensitivity, and the estimated size and cost of the envisioned bomb sniffer.

6.1 Locations and Speed of Chemosensing

The merits of various locations for bomb search in airports and aircraft have been discussed in detail in the previous studies. The choice of the locations depends in part on the speed with which the detection can be performed.

The process investigated in this study consists of adsorptive or absorptive extraction of the vapors from a large volume of air and a rapid analysis of the captured substances for the presence or absence of nitroglycol, DNT, and perhaps additional components related to the explosives, e.g., nitroglycerin and TNT. In this study, analysis in time intervals or the order of 20 to 75 sec was possible. The processing of the information is electronic and very fast, in fractions of seconds. Air sampling has not been studied for its rapidity, but 0.3 liters of air per minute could be passed through the capillaries used in the laboratory work. Increasing the sampling rate to 100 liters/min or 3.5 cu ft/min should not be too difficult, even with appropriately sized capillaries in parallel, and rates several times the latter could be achieved with other geometric arrangements. If the sensitivity of the detection method is increased, lesser samples may suffice. Tentatively, the detecting process time may be estimated optimistically at 1 to 2 min, although there are no basic reasons why shorter times would not be possible.

With a sampling and detecting time of 1 min, a search of individual luggage pieces and passengers boarding a jetliner is not feasible, except selectively or with a battery of detectors. A comprehensive search would be best conducted on a mass inspection basis, inspecting all luggage pieces simultaneously, or in groups. Similar procedures would have to be applied to passengers.

In selection of the inspection point, several factors must be considered. In general, the concentration of the vapor of the explosive should be allowed to stay as high as possible in the air that is sampled. Therefore, the smaller the enclosure from which the air is sampled, the better. Also, since the vapor pressures decrease with temperature, the enclosure should not be too cold. If the temperature is -10°C (14°F), the vapor pressure of nitroglycol is 30 times lower than at room temperature (Figure 1) and the difficulty of detection is increased.

On the basis of these considerations, the luggage is best inspected either in a small intermediate storage compartment or in the luggage compartment of the plane. The latter location is less desirable in particularly cold weather. The passengers and the hand-carried luggage are best inspected either in a lounge, after passing the ticket check and before boarding the aircraft, or in the airliner cabin shortly before the takeoff. A lounge is unlikely to contain more passengers per volume unit than an

airliner cabin. Hence, other aspects -- convenience, cost, technical feasibility -- become more important in deciding the location for the inspection of passengers. Except for the possibility of low temperatures in the airliner's luggage compartment, the location of the inspection equipment directly on the airliner seems to be the simplest and most suitable. Then the checkout system can be arranged as part of the aircraft equipment, and a check for the explosives aboard the aircraft can be one of the steps in the checkout procedure. The desensitizing effect of lower temperatures in the luggage compartment may be compensated by much smaller air volume as compared with the cabin and by more efficient sampling, which is feasible in a volume that is not inhabited. Faster air circulation, stronger or repeated pressure changes, etc. can be used in absence of passengers and personnel.

6.2 Prospects for Sensitivity

The sensitivity of the chemosensing process must be the largest when the bomb is in a relatively small container -- carton, briefcase or under-the-seat suitcase -- in the aircraft passenger cabin. Then the bulk of the bomb vapors, e.g., of nitroglycol, are enclosed by the container and must be pulled out into the cabin space where the sampling occurs; otherwise the container must stay in the cabin long enough for the vapor to leak out and accumulate. A hermetic container would be very unusual and would require exceptional technical competence. All usual containers are sufficiently leaky; part of the air can be pulled out by a manipulation of cabin pressure, unless later studies show that within 5 to 10 min a sufficient amount of vapor will leak into the cabin air from common containers.

The manipulation of the air pressure may consist of reducing the pressure somewhat, e.g., by 1 to 2 psi, or by alternate increase and decrease of the pressure. In further work, the feasibility of depressurizing or pressure cycling must be explored with the assistance of aircraft specialists.

An estimate of the sensitivity requirement is as follows. A typical small container is a large briefcase, 12 by 16 by 2 in. This is a volume of approximately 5,000 cm³. One half of its volume, when packed, is assumed to be air. If the pressure is reduced by 2 psi, or first increased by 2 psi and then released, approximately

$$\frac{5000 \times 2}{2 \times 15} = 330 \text{ cm}^3$$

will be pulled into the cabin air. On the basis of experiments conducted in this study on vapor pressures of nitroglycol in leaky containers with dynamite, it can be estimated that approximately 10⁻⁷ g of nitroglycol will be now in the cabin. Larger containers

or repeated pressure cycling will increase the amount of nitroglycol in the cabin air. The volume of pressurized space in a jetliner is typically 15,000 cu ft. If 15 cu ft of air is sampled and the process of sampling and injection into the chemosensing sniffer is fully efficient, 10^{-10} g must be sensed. This is somewhat lower than the sensitivity of the tentative procedure developed in this study, in which amounts down to 2×10^{-10} g were detected. Sampling of larger amounts of air may be possible, and improvements in the sensitivity of the chemosensing process by a factor of 10 to 100 appear feasible.

Thus, as far as the sensitivity is concerned, a dynamite bomb detector is close to the range of technical feasibility.

6.3. Size, Weight, and Cost

One step in the envisioned bomb detection procedure will be concerned with transfer of some air from closed luggage, etc. to the cabin or luggage space atmosphere. This step can utilize some of the airliner's air system and operate through pressure cycling, unless later studies show that this is not necessary.

The bomb-sniffer itself requires the following principal components. The sampling section can consist of an adsorptive or absorptive duct register and a blower, which could pull 10 to 100 cu ft/min through the register. The flashing section will operate electrically and perhaps will need a transformer to produce low-voltage high current. The carrier gas section will need a supply of inert gas, such as argon or helium, but the gas expenditure will not exceed several liters per hour. Solenoid valves, sorbent cartridge, etc. will be needed in the carrier gas section to connect it to the sampling and the analytical section. The partition column section is a short capillary equipped with a thermostatted heating block. The electronics section will consist of the electron-capture detector, stabilized potential supply, low-noise electrometer, display subsystem, and a timing mechanism that coordinates the operation of the sections.

All these sections and subsystems are within the state of art, and none requires unusually heavy, bulky, or exceptionally costly items. The development of a reliably operating bomb-sniffer from the proposed concepts and components is still a complex task, and the total size, weight, energy demand, and cost are difficult to estimate. As a gross approximation, 1 cu ft of space may suffice. A weight of 50 lb is probably in the proper order of magnitude. The cost of the standard items in the system will not exceed \$1,000 to 2,000, but several components must be developed specifically for the bomb-sniffer, so that the total cost of the device, if it is produced in larger numbers after development, can be several times this figure. The above statements should be considered merely as the best guesses at the present time.

7.0 PROJECT ADMINISTRATION

The principal investigator on this program was Dr. Andrew Dravnieks, aided by Harold S. Weber, Paul Ase, Joan Frerichs, and Phillip Trotter. The data were recorded in IIT Research Institute logbooks C14300, C14371, C14730, C14757, C15055, C15239, and C13234.

CONCLUSIONS

The study has established that:

- (1) several common explosives emanate small amounts of characteristic vapors.
- (2) the presence of these explosives can be noticed by detection of their characteristic vapors,
- (3) the presence of most of the investigated common substances and odors, including jet fuel vapors, does not seriously interfere with the detection of these explosives,
- (4) in the present state of technology the electron-capture detector is preferable to the contact - potential devices for the proposed task, and finally,
- (5) reasonable prospects exist for escalation of the evolved techniques to a level that may make it possible to detect explosives in more difficult geometries.

Respectfully submitted,

IIT RESEARCH INSTITUTE

Andrew Dravnieks
Andrew Dravnieks
Scientific Advisor

Approved by:

Eli S. Freeman
Eli S. Freeman, Manager
Physical Chemistry Research

APPENDIX
EXPERIMENTAL LABORATORY EQUIPMENT

KEY TO FIGURE A-1
GAS CHROMATOGRAPHIC SYSTEM

- P Power supply for direct heating of narrow tube, T, for rapid sample injection.
- T Sampling tube in system flow line.
- F Column-heating furnace in raised position.
- C Packed 10-ft column wound into a spiral about 3 in. x 3½ in.
- R Regulator and temperature programmer for furnace, F.
- I Heated injection block for samples taken by syringes, S.
- S Syringes (from left to right) 10 microliter, 1 cm³, and 3 cm³, used in direct air sampling.
- E-1 Amplifier for flame-ionization detector.
- E-2 Amplifier for electron-capture detector.
- A Dual pen recorder for simultaneous measurement of output of E-1 and E-2.

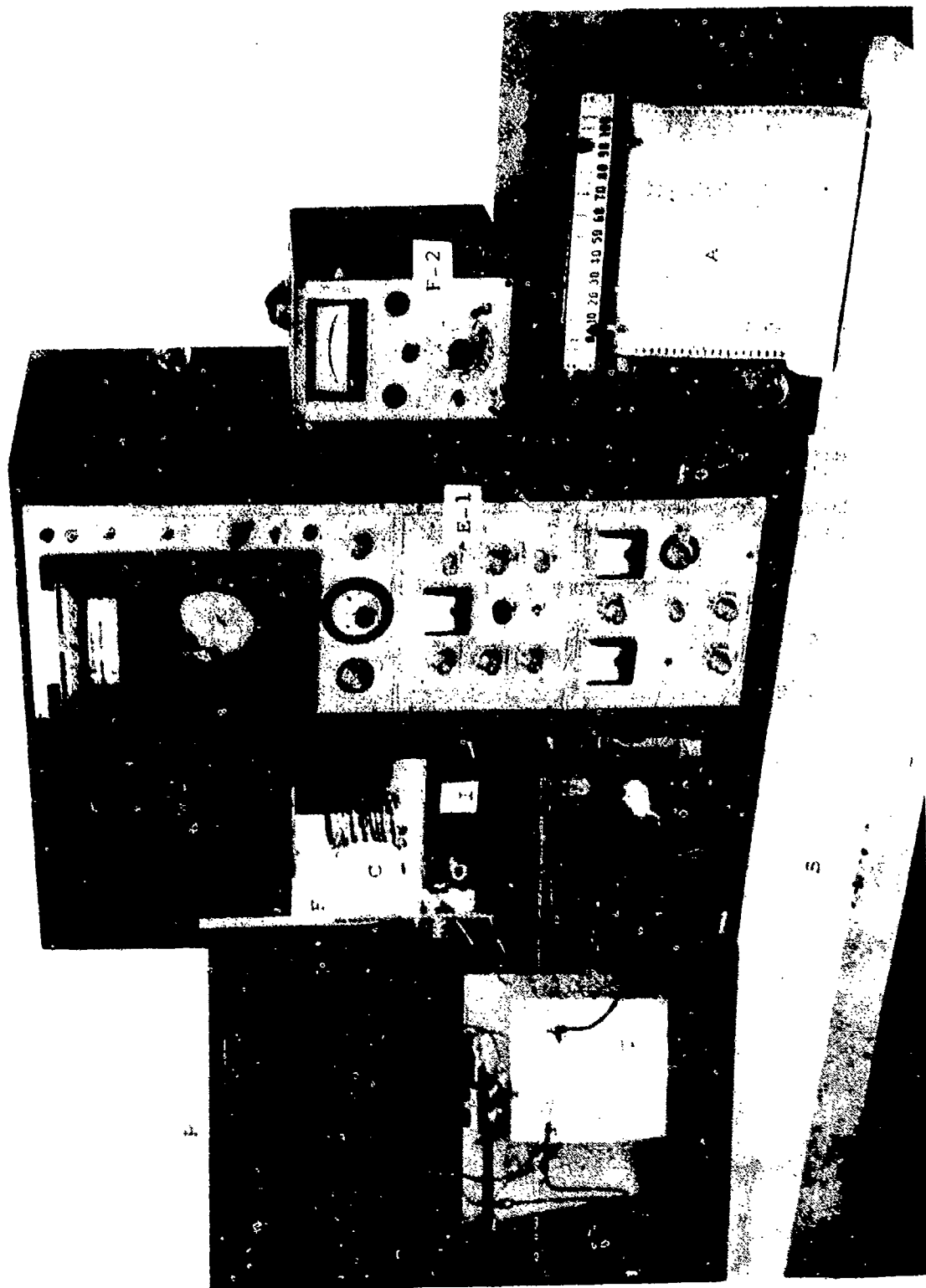


Figure 1
CRYPTOGRAPHIC SYSTEM

KEY TO FIGURE A-2

DETECTION OF EXPLOSIVE VAPORS IN A DESICCATOR
WITH COMMON OBJECTS

- D Desiccator with $\frac{1}{2}$ -lb stick of Gelamite-1 wrapped in wax paper and tin of shoe polish.
- C Lipstick, insect repellent, hairspray, purse with Vibronite B explosive, keys, coins, and playing cards, as common objects used in desiccator experiments.
- T Dewar for dry ice used to trap vapors drawn from desiccator.
- M Manometer to measure pressure reduction.
- B Back-diffusion trap to prevent water from aspirator, P.
- P Water aspirator to pump out desiccator.

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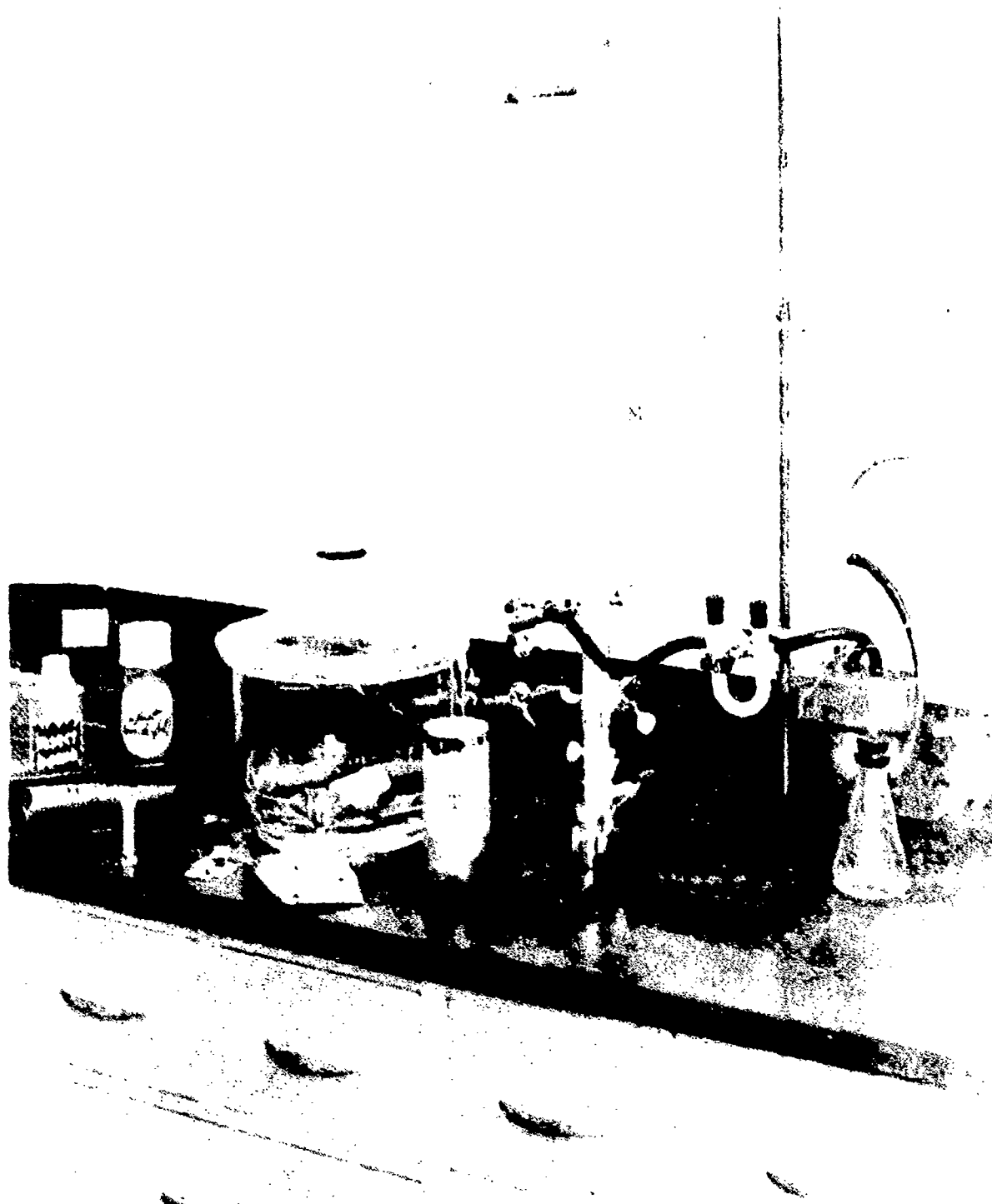


Figure A 2

DETECTION OF EXPLOSIVE VAPORS IN A DESICCATOR
WITH COMMON OBJECTS

KEY TO FIGURE A-3

DETECTION OF GELAMITE-1 IN SUITCASE WITH CLOTHES
AND LIKELY OBJECTS

- S Suitcase containing battery, wire, towels and other clothing, and $\frac{1}{2}$ -lb stick of Gelamite-2.
- T 1/32-in. ID x 77-in. long tubes used to trap vapors in cooled Dewar, D, or uncooled in open air.
- D Dewar with dry ice coolant.
- M Manifold for simultaneous sampling at up to 6 different points.
- P Mechanical vacuum pump.

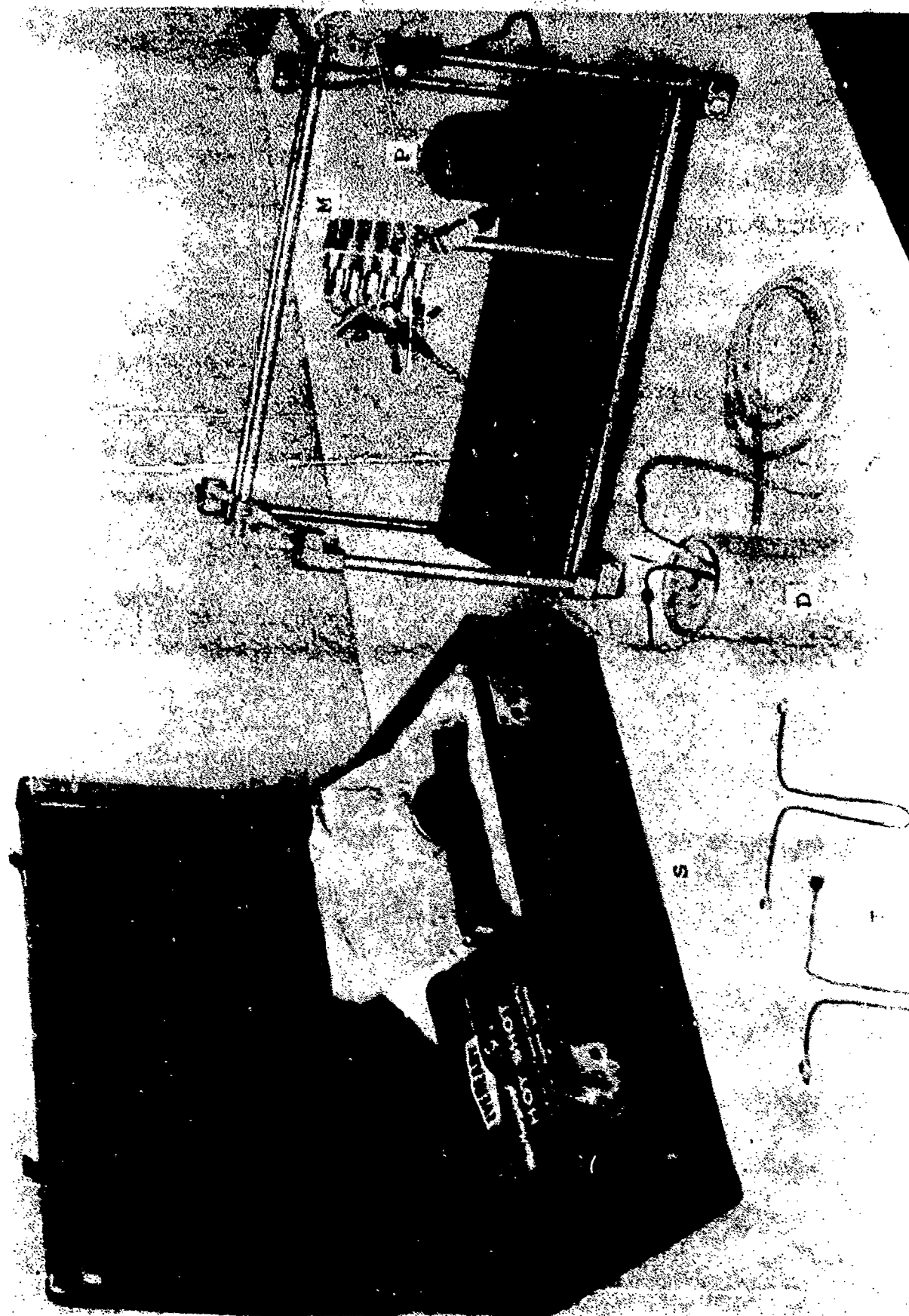


Figure A-2

DETECTION OF HAZARDOUS MATERIALS WITH CLOTHES AND LIKELY OBJECTS

KEY TO FIGURE A-4

CONTACT-POTENTIAL APPARATUS FOR POLAR VAPOR DETECTION

- R Rack for gas flow control and vapor generation train.
- G Gas flow control valves.
- T Thermostat to supply constant-temperature water to contact-potential apparatus, M.
- M Contact-potential block containing vibrating membranes, electrical connections, and gas inlet ports.
- B Contact-potential balancing unit.
- C Cathode-ray oscilloscope used to judge balancing null point.

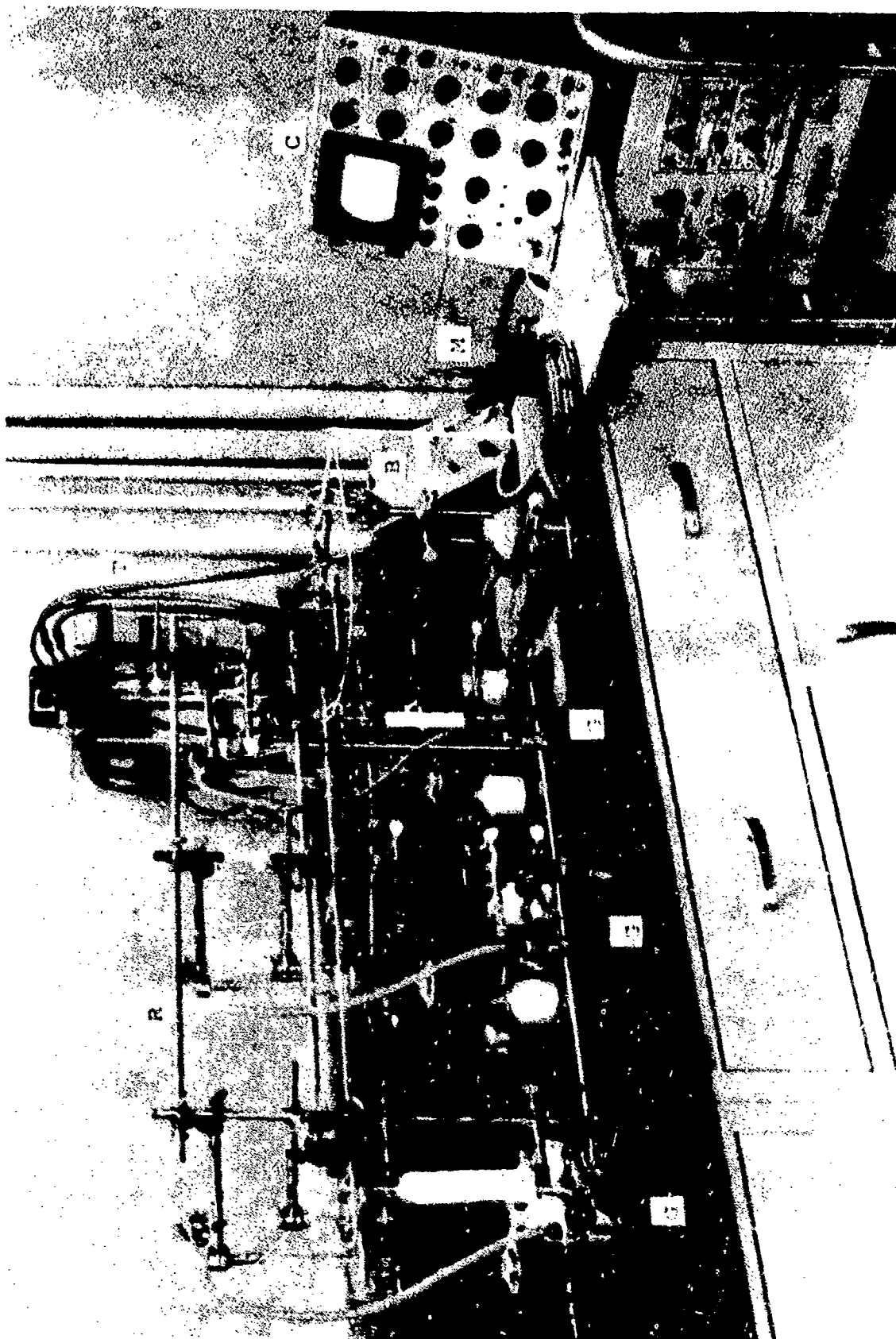


FIGURE 4
POLAR VAPOR DETECTION APPARATUS

GLOSSARY OF UNCOMMON TERMS

Absorption	dissolution of a vapor in the bulk of liquid, grease, or solid
Adsorption	retention of vapor molecules at the surface of a solid by surface forces.
Aliquot	a measured fraction of a sample or solution
Benzene ring	molecular structure consisting of six carbon atoms joined in a ring. In benzene, one hydrogen atom is attached to each of the carbon atoms; these hydrogen atoms can be substituted by nitro and other groups to form explosive molecules such as DNT and TNT.
Calorie	measure of heat energy; one calorie will heat one gram of water one degree centigrade.
Calorimetric measurement	measurement of heat consumed or released by substances due to temperature or chemical changes.
Carotenes	vitamin A-like substances with long chains of alternated single and double bonds between the carbon atoms of the chain.
Carrier gas	inert gas used to sweep vapor molecules through a gas-chromatographic column to a detector.
Charge-transfer complex	chemical compound formed by combination of electron-donor and electron-acceptor molecules; frequently has distinct color and high dipole moment. The compound is formed by the transfer of an electron from the donor to the acceptor.

Chemosensing	sensing or detecting objects through the detection and identification of the chemical vapors that emanate from the objects.
Column	in gas chromatography, a long narrow tube of liquid or grease coated inside with a thin film, or frequently packed with coated particles, used to separate vapor and gas mixtures.
Contact-potential detector	an electrical device used to measure the difference in the energy states of electrons of two metals. The relative energy states are influenced by the surface environment of the metals and are altered by adsorbed vapors.
Convection, in air	turbulence in air caused by natural movements of air, principally because of local differences in temperature.
Counterdiffusion	diffusion of molecules against the direction of flow of a gas in a tube.
Debye unit	a unit measure of the dipole moment of a molecule.
Desorption	evaporation of a material from a surface -- opposite of adsorption.
Detector	device that detects the presence of substances passing through it, usually by a change in electrical signal.
Diffusion, in air	movement of molecules of a vapor, with respect to air molecules, from higher to lower concentration.
Dinitrotoluene (DNT)	co-present with trinitrotoluene (see TNT) or used in commercial explosives as an explosion regulator.

Dipole moment

an electric moment -- the product of a charge and a distance -- that results from noncoincidence of the electrically positive and negative centers in a molecule.

Electron acceptor

a molecule that has a tendency to withdraw electrons from other molecules and become a negative ion by incorporation of the electron into its own electronic structure.

Electron-capture detector (ECD)

an electrical device used to detect molecules that easily form negative ions by capturing free electrons. The electrons are generated in a small volume by radioactive hydrogen (tritium) stored in the form of titanium hydride.

Electron donors

molecules capable of giving, at least partially, an electron to another molecule, thus becoming positive.

Electronic structure

the disposition of electrons around the positive nuclei in the substance or molecule.

Ethylene glycol dinitrate (EGDN)

a more scientific name for nitroglycerol.

Flame-ionization detector

a device used to detect molecules in a carrier gas by measuring the current produced from the ions that are formed in a small hydrogen-air flame as the molecules enter the flame

Gas chromatography

a method of chemical analysis and identification of molecular species. Complex mixtures of volatile compounds are separated by passage through a long column with detection and recording by some means at the column outlet.

Heat of fusion

heat required to melt (fuse) a solid.

Heat of sublimation	heat required to vaporize a solid.
Heat of vaporization	heat required to vaporize a liquid.
Ideal mixtures	liquid mixtures in which partial vapor pressures of the components are proportional to their concentration in the liquid.
Infrared	invisible light (electromagnetic radiation) in the wavelength range 0.7 to about 100 microns.
Intermolecular interactions	molecular forces that cause attraction or repulsion between molecules and can lead to deviations from the law of ideal mixtures.
Ion	a molecule or atom with an electric charge.
Ionization	process of making ions from molecules or atoms by attaching or withdrawing electrons, or by splitting a molecule into positively and negatively charged parts.
Kinetic factors	factors that determine rates, e.g., in processes that depend on air movement factors such as pressure drops, diffusion, convection, etc.
Microgram (μg)	one-millionth of a gram; 10^{-6} g.
Microliter (μl)	one-millionth of a liter; 10^{-6} liter; one-thousandth of a cubic centimeter.
Micron	unit of length, the one-thousandth part of a millimeter.
Microwave	a form of invisible light (electromagnetic radiation) with a very long wavelength (about 1 mm).
Milligram (mg)	one-thousandth of a gram; 10^{-3} g.

Millimeter of mercury (mm Hg)	unit of pressure; 760 mm Hg = 14.7 psi.
Mole	the quantity of a chemical substance that has a weight in grams numerically equal to the molecular weight.
Molecular species	a molecule; an organized grouping of two or more atoms that form a stable, usually fairly rigid, structure.
Nanogram (ng)	one-billionth of a gram; 10^{-9} g.
Nitrate group	the grouping of three oxygen and one nitrogen atom with the arrangement $\begin{array}{c} \text{O} \\ \parallel \\ -\text{O}-\text{N} \\ \parallel \\ \text{O} \end{array}$
Nitroglycerin	a common component of dynamites and some smokeless powders; it consists of nitroglycerin proper and 20 to 80% nitroglycol.
Nitroglycol (EGDN)	a common component of nitroglycerin, used in explosives.
Nitro group	the grouping of two oxygen and one nitrogen atom with the arrangement $\begin{array}{c} \text{O} \\ \parallel \\ -\text{N} \\ \parallel \\ \text{O} \end{array}$
Partial pressure	the vapor pressure of a substance in a mixture of other vapors or gases.
Partition coefficient	the ratio of the concentration of a vapor in the stationary (liquid) phase to that in the vapor phase as it passes through a gas chromatographic column.
Phase	general term for the state of aggregation of a substance; can be solid, liquid, or gaseous.
Polar molecule	a molecule that possesses a dipole moment or permanent over electrical charge separation, with no net electrical charge.

Polyglycol	a polymeric material with many alcohol functional groups, i.e., -OH groups.
Polynitro compounds	a compound having two or more nitro groups: TNT, DNT, etc.
Raman scattering	a change in frequency undergone by a portion of light that has been scattered in passage through a transparent liquid, solid, or gas whose molecular characteristics determine the amount of change.
Retention time	time interval required for any molecular species to pass through a gas-chromatographic column.
Stationary phase	a semiliquid material supported on solid particles in a gas-chromatographic column or on walls of the column. It remains stationary as the vapor-laden carrier gas passes over it and momentarily retains some of the vapor, thus delaying its passage through the column.
Sorption	retention of a vapor by a substance or a solution; it can occur through <u>absorption</u> and <u>adsorption</u> .
Sublimation	passage of molecules directly from the solid to the gaseous phase without becoming liquid, e.g., evaporation of dry ice.
Thermodynamic factors	heat-, temperature-, and concentration-dependent factors that determine the amount of vapor of any species that will exist around an explosive.
Trinitrotoluene (TNT)	a component of most military explosives.
Vapor	a molecular species in the gaseous state.
Vapor pressure	the pressure exerted by molecules in the gaseous state on unit wall area.

REFERENCES

1. "Feasibility Study of Methods of Protecting Commercial Aircraft against Inflight Bombing," Stanford Research Institute, for Air Transport Association, Final Report, 1960.
2. "Rapid Identification of Radioactive Tracers in Detonator Caps with Large Volume Liquid Scintillation Detectors," The Catholic University of America, for United States Atomic Energy Commission and Federal Aviation Agency, 1963.
3. "Bomb Detection System Implementation Analysis," Southern California Laboratories of Stanford Research Institute, for Federal Aviation Agency, 1964.
4. R. W. Van Dolah and M. J. Hanna, "Initiation of Bombs Without the Use of Blasting Caps," U.S. Bureau of Mines, U.S. Dept. of the Interior, Project No. 11-3273.7, Report No. 3913, Feb. 10, 1964.
5. "Properties of Explosives of Military Interest," Ordnance Corps, U.S.A. Pamphlet ORDP 20-177, Washington, D. C., May 1960.
6. Grimm, M. G., Gunther, M., and Tittus, H., Z. Physik. Chem. B14, 169 (1931).
7. Brown, F. S., J. Chem. Soc. 127, 345 (1925).
8. Rheinbolt, H., Hennig, K., and Kircheisen, M., J. Prakt. Chem. 111, 242 (1925).
9. Kofler, A., Z. Physik. Chem. A190, 287 (1942).
10. Weygand, D. and Siebenmark, T., Ber. Deut. Chem. Ges 73B, 765 (1940).
11. Good, M., Major, A., Nag-Chandhuri, J., and McGlyn, S. P., J. Am. Chem. Soc. 83, 4329 (1961).
12. Tsubomura, H. and Lang, R. P., J. Am. Chem. Soc. 83, 2085 (1961).
13. Drago, R. S., Carlson, R. L., Rose, N. J., and Wenz, D. A., J. Am. Chem. Soc. 83, 2572 (1961).
14. McCoullough, J. D. and Zimmerman, I. C., J. Phys. Chem. 65, 888 (1961).

15. Pullman, B. and Pullman, A., Quantum Biochemistry, Interscience Publishers, New York, pp. 435, 550 (1963).
16. Andrews, L. J., Chem. Rev. 54, 713 (1954).
17. Briegleb, G., Elektronen Donator-Akzeptor Komplexe, Springer Verlag, Berlin, 1961.
18. Dravnieks, A. and Weber, H., "Sensitivity Limitations in Detection of Contaminants in Air," presented at the Conference on Surface Effects, Brookings Institution, Washington, D. C., July 1964.
19. Dravnieks, A., in Encyclopedia of Electrochemistry, Reinhold Publishing Company, 1964, p. 236.
20. Burchfield, P. H. and Storrs, E. E., "Gas Chromatography," Academic Press, New York, (1962).